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Continuous, Ionic Liquid-Catalysed Propylation of Toluene in a Liquid-Liquid Biphasic Reaction Mode using a Loop Reactor Concept

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Abstract: Acidic ionic liquids of the type [cation][bis(trifluoromethanesulfonyl)imide anion]/aluminium trichloride {[cation][$(CF_3SO_2)_2N$]/$AlCl_3$} have been applied to realise for the first time a continuous Friedel–Crafts alkylation reaction in liquid-liquid biphasic reaction mode using a loop reactor concept. Exemplified for the continuous propylation of toluene we have proved that the acidic catalyst layer is successfully immobilised over at least 18 h in the loop reactor. After 8 h time-on-stream, a steady state has been reached followed by at least 10 h time-on-stream without any loss of activity or change in selectivity. Our results reveal the high potential of this class of acidic ionic liquids in continuous arene functionalisation reactions.

Keywords: alkylation; aromatic substitution; continuous operation; immobilisation; ionic liquids

Introduction

Electrophilic aromatic substitution reactions – especially the group of Friedel–Crafts reactions – are among the most important reactions for the preparation of alkylated arenes in industry. Catalysts for Friedel–Crafts alkylation reactions industrially in use are Lewis acids like $AlCl_3$, $FeCl_3$, $TiCl_4$, $ZnCl_2$, SbF_5 and BF_3 as well as Brønsted acids like HCl, H_2SO_4, H_3PO_4 or HF.

One important way in which Friedel–Crafts alkylation reactions are carried out technically is the liquid phase reaction with a homogeneously dissolved $AlCl_3$ catalyst (red-oil). In this process, the catalyst is removed from the formed products by a washing procedure with water and thus a large amount of waste water is produced. Moreover, the washing process leads to the hydrolysis of the $AlCl_3$ catalyst which cannot be recycled and the formed alumina is either disposed off or finds applications in, e.g., street building.

A very promising method for the immobilisation of acidic catalysts is being offered by ionic liquids. Ionic liquids represent a new class of solvents which consist only of ions and are liquid at temperatures below 100 °C.[1–3] In recent years, ionic liquids have attracted much interest as catalysts and alternative solvents for chemical transformations.[4] Chloroaluminate ionic liquids were the first Lewis acidic ionic liquids to be studied in detail[5] and are still among the best investigated ones. Since their discovery, these "first generation" ionic liquids have been widely used in form of their acidic compositions (ratio [cation]Cl/$AlCl_3 < 1$) as catalysts for liquid-liquid biphasic Friedel–Crafts reactions and similar chemistry making use of the pronounced miscibility gap between the ionic liquid and the aromatic feedstock/product mixture.[6] As a general conclusion from all acid-catalysed reactions with chloroaluminate ionic liquids it can be stated that the acidity of the ionic liquid depends on the amount of $AlCl_3$ in the mixed [cation]Cl/$AlCl_3$ system. The higher the amount of $AlCl_3$, the higher is the acidity and hence the catalytic activity of the ionic liquid. However, the amount of $AlCl_3$ in the chloroaluminate system is effectively limited by the liquid range of the ionic liquid to a maximum molar ratio of 2 mol $AlCl_3$ per mol of [cation]Cl.

Recently, we have reported that ionic liquids of the type [cation][$(CF_3SO_2)_2N$] are able to dissolve much larger amounts of Lewis acids {e.g., up to 5 equivalents of $AlCl_3$ per mol of "matrix ionic liquid" [cation][$(CF_3SO_2)_2N$]}.[7] In addition they form biphasic systems with many organic product mixtures so that the same possibility of a multiphasic reaction mode can be applied as known from the chloroaluminate systems. In this way easy product isolation and catalyst recovery can be realised. Most interestingly, in the system [cation][$(CF_3SO_2)_2N$]/$AlCl_3$ the ionic liquid can be seen as a true "matrix" for the $AlCl_3$. The valuable matrix ionic liquid can be recycled even in cases where an aqueous work-up would become necessary after prolonged use of the acidic ionic liquid. This is due to the hydrolytic stability and the hydrophobic character of the $(CF_3SO_2)_2N$ anion. In contrast, the organic cation is usually lost into the aqueous medium if acidic ionic liquids of the type [cation]Cl/$AlCl_3$ are worked-up hydrolytically.

Today, a detailed literature survey reveals many recent publications describing acidic ionic liquid catalysts in Friedel–Crafts alkylation reactions.[8–11] Most of them also deal with the recovery and reuse of the acidic phase in form of repetitive batch mode experimentation. Several recycling experiments were described to be affected by a slight loss of activity,[12] especially at higher recycling rates. This may have to do not only with intrinsic catalyst instability but also with the specific conditions of the repetitive batch experiments. This methodology suffers from the necessity to completely recover the catalyst phase after a run for proper re-injection into a new batch. Loss of catalyst phase and also contamination with traces of humidity are usually inevitable at least to some extent in this procedure and this leads to deactivation due to the extreme hygroscopic nature of the Lewis acidic ionic liquid systems.

In the present paper we report for the first time a Friedel–Crafts alkylation using acidic ionic liquids as the catalyst phase that is immobilised in a loop reactor under continuous reaction/extraction conditions. Figure 1 shows the particular reaction under investigation (here schematically represented in a stirred tank reactor), namely the propylation of toluene using ionic liquids of the general type $AlCl_3$/[cation][$(CF_3SO_2)_2N$] (ratio > 1.5) being applied as the catalyst phase. Our aim was to gain from such a study a more detailed insight into the technical potential of continuous Friedel–Crafts alkylation reactions with ionic liquids.

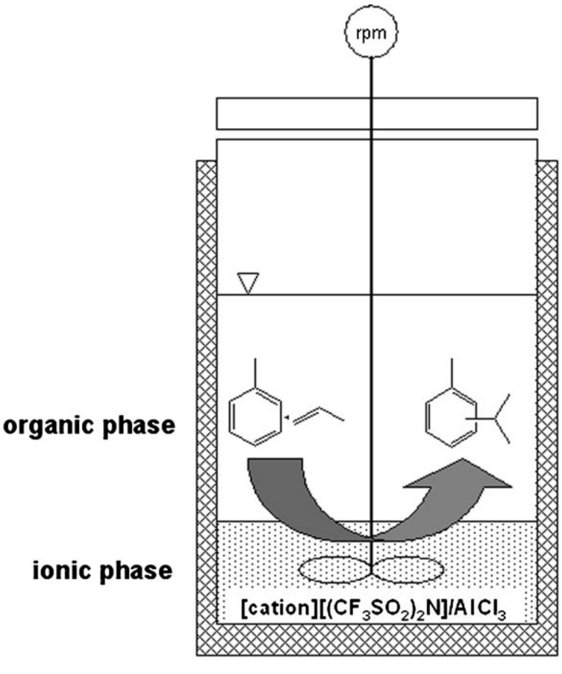

Figure 1. Isopropylation of toluene in ionic liquids.

Results and Discussion

Preliminary Experiments in a Pressureless, Semi-Batch Reactor

Influence of the $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] Ratio of the Applied Ionic Liquid

First, we aimed to understand influencing factors in the catalytic system under investigation. Therefore, the propylation of toluene was investigated in a batch reactor system with propene bubbled through a catalyst/organic biphasic system with vigorous stirring (for details see Experimental Section) to determine the influence of the matrix ionic liquid to $AlCl_3$ ratio on the activity and selectivity of the reaction. Figure 2 shows the results for the system $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] ([BMIM] = 1-butyl-3-methyl-imidazolium) in the composition range of 0.65 to 3.68 in this pressureless apparatus at 15 °C.

A clear tendency of the selectivities could be observed with a maximum yield of *meta*-cymene at highest acidities. For molar ratios $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] < 1.5 no catalytic activity was found. We attribute this observation of a required "minimum acidity" in the specific system $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] to the presence of different anion species depending on the amount of $AlCl_3$ added to the matrix ionic liquid.[13] Only a molar ratio of $AlCl_3$ greater than 1.5 forms anionic species (dimeric and trimeric species are also assumed) acidic enough to catalyse the propylation of toluene. Increasing the amount of $AlCl_3$ leads to an increased formation of highly acidic species in the catalyst system accompanied by a higher selectivity to *m*-cymene formation (clearly beyond the analytical error).

Variation of the Total Amount of Catalyst System

Since the amount of matrix ionic liquid [BMIM][$(CF_3SO_2)_2N$] was kept constant in these experiments, the total amount and volume of the catalyst phase were changed with different amounts of $AlCl_3$ added to the catalyst system. The next set of experiments aimed to make sure that the selectivity of the reaction was not a function of the total volume of the catalyst phase in the experiment. Therefore, further alkylation reactions were carried out with a constant molar ratio

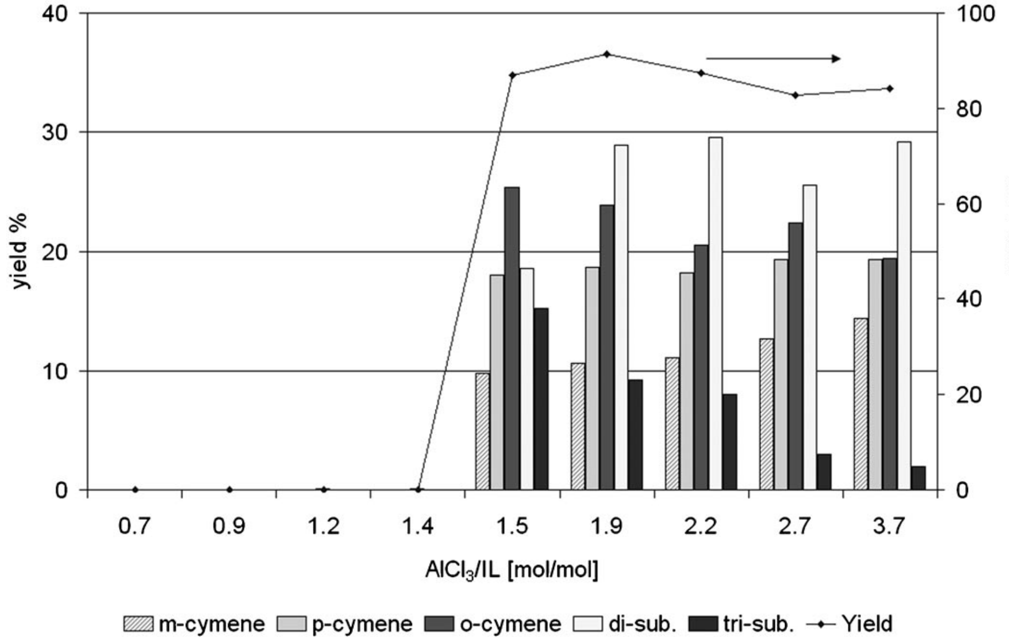

Figure 2. Yield of products (based on propene) obtained with different AlCl$_3$/[BMIM][(CF$_3$SO$_2$)$_2$N] ratios of the applied ionic liquid catalyst phase. *Conditions:* $T=15\,°C$; reaction time: 15 min; propene = 7 NL/h (0.4 mol/h); n(toluene) = 0.27 mol, n([BMIM][(CF$_3$SO$_2$)$_2$N]) = 0.015 mol).

Table 1. Influence of the total amount of catalyst system AlCl$_3$/[BMIM][(CF$_3$SO$_2$)$_2$N] (at constant ratio of 3.2) on the product distribution.[a]

m(AlCl$_3$/[BMIM][(CF$_3$SO$_2$)$_2$N]) [g]	Yield [%]					Conversion [%]
	meta-cymene	*para*-cymene	*ortho*-cymene	di.-substituted	tri-substituted	
1.6	11.8	18.2	21,7	26.7	5.1	83.6
4.4	11.1	18.2	21.4	31.1	8.3	90.0
8.9	11.4	18.1	20.5	32.8	5. 7	88.8

[a] *Conditions:* $T=15\,°C$; reaction time: 15 min; propene = 7 NL/h (0.4 mol/h); n(toluene) = 0.27 mol.

AlCl$_3$ to matrix ionic liquid [BMIM][(CF$_3$SO$_2$)$_2$N] but with different amounts of total catalyst system (Table 1).

As expected, we could clearly show that the ratio of AlCl$_3$ to [BMIM][(CF$_3$SO$_2$)$_2$N] and thus the ionic liquid's acidity is decisive for the selectivity change observed (see Figure 1) and not the total amount of acidic catalyst phase in the reactor.

Recycling Experiments in Repetitive Batch Mode

The main precondition to apply the new catalyst system in a continuous liquid-liquid biphasic operation is the sufficient stability of the catalytic system over time under the conditions of an intensive extraction of the acidic catalyst phase by the organic feedstock/product phase. For a preliminary check of this system's stability, the ionic catalyst system was separated from the organic compounds after the reaction time of 20 min and reused for a next alkylation reaction under identical conditions. In order to remove organic components completely from the ionic liquid, the catalyst was extracted three times with cyclohexane prior to reuse. The yields of products over the five recycling experiments are shown in Figure 3.

Figure 3 shows an almost constant product distribution for the monoalkylated toluenes over all six cycles. No loss of activity could be observed, so that the application in a continuous rig appeared to be justified. It should be noted that in this experiment the molar ratio between toluene and propene was higher than in previous experiments resulting in slightly different selectivities with less formation of di- and trisubstituted products. Increasing the molar ratio of toluene with respect to propene also resulted in a higher

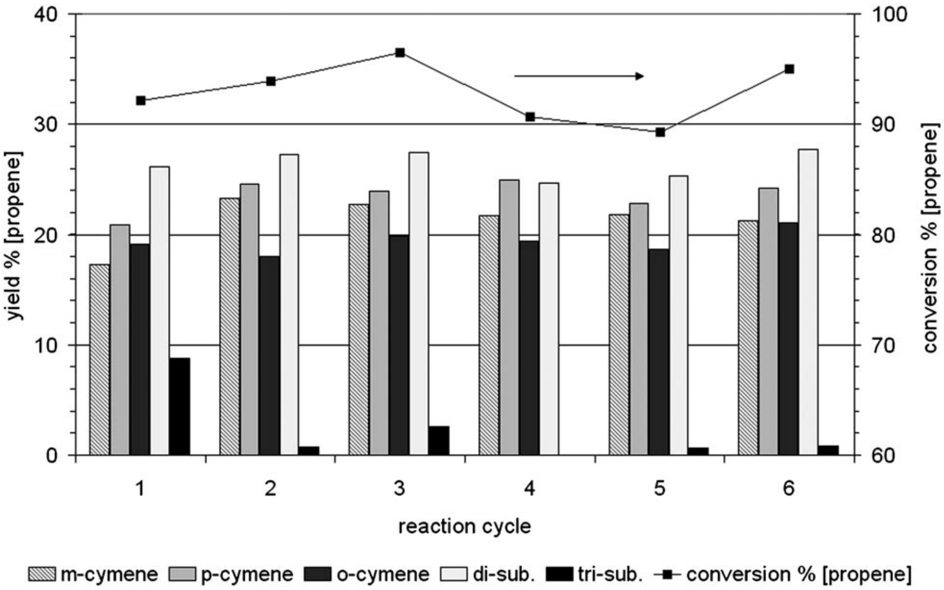

Figure 3. Recycling experiments of the ionic catalyst system. *Conditions:* $T = 15\,°C$; reaction time = 20 min; propene = 7 NL/h (0.4 mol/h); n(toluene) = 0.46 mol, n([BMIM][$(CF_3SO_2)_2N$]) = 0.015 mols), n([BMIM][$(CF_3SO_2)_2N$]/$AlCl_3$) = 1/3.3.

yield towards *m*-cymene in the monoalkylated products as can be seen by comparing the data with those presented in Table 1 and Figure 2.

Continuous Experiments in a Loop Reactor with Internal Phase Separation

To further check the technical potential of the new catalyst system [BMIM][$(CF_3SO_2)_2N$]/$AlCl_3$, the operational lifetime of the catalyst system was investigated under the realistic conditions of a continuous operation in a loop reactor. In contrast to the semi-batch experiments described above, the reaction is carried out under pressure in the loop reactor to ensure that propene is processed as a liquid phase with no reactive gas phase present in the reactor. A schematic view and a picture of the applied loop reactor system are shown in Figure 4, a detailed description of the operating method can be found in the Experimental Section.

Prior to the catalytic reaction, the ionic catalyst solution was placed into the reactor loop. The organic feedstock components were continuously fed and – after passing an internal phase separator – the products were continuously discharged. Thus, in contrast to the use of an external separation, all catalyst was always present in the loop reactor. This allowed direct investigation of the catalyst reactivity by analysis of the isolated products. In the loop reactor, the liquid-liquid biphasic reaction mixture was circulated by a circulation pump with high flow rates ($4\,L\,min^{-1}$). Under these conditions the two static mixers in the reactor loop provided an efficient dispersion of the ionic catalyst solution in the organic phase. Two heat exchangers in the loop ensured full temperature control. As the loop circulation flow is large compared to the continuous inflow of feedstock and outflow of products, the system in use was characterised by a residence time distribution similar to a CSTR (continuous stirred tank reactor). A more detailed residence time distribution investigation revealed that the data of a step function experiment could be well fitted to a CSTR reactor showing 11% of short circuit flow and 31% of the flow not fully back-mixed (e.g., due to dead volume in the separator).

Figure 5 shows product yield (with respect to propene) and amounts of different products formed for a selected example of our continuous catalytic runs over 18 h at 50 °C.

The yield of alkylated products reached a stable value after four hours time-on-stream (corresponding to about 7 residence times) and stayed constant for the next 14 h. No deactivation of the catalyst was observed after 18 h of operation when the continuous reaction was liberally stopped. However, an interesting shift in product selectivity was found during the first 8 h of operation with decreasing selectivity for *meta*-cymene (from 45% to 15% during the first 8 h) and a pronounced rise in the formation of *ortho*-cymene (from 10% to 20% within the first 10 h). Remarkable, the product distribution remained essentially unchanged between 10 h and 18 h time-on-stream with selectivity to monoalkylated products of about 55%. Compared to our semi-batch results the different initial selectivity can be explained by the much higher initial molar ratio of toluene with respect to propene (the reactor was completely filled with tolu-

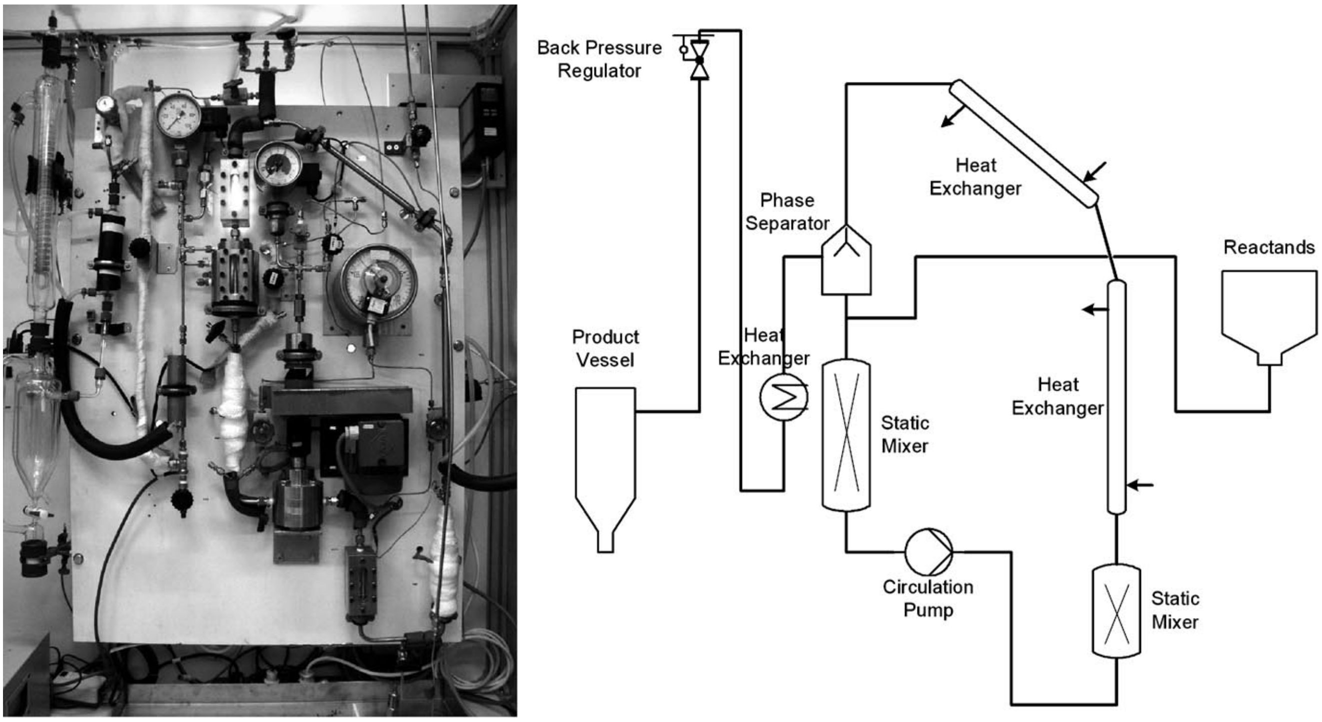

Figure 4. Continuous loop reactor used for the isopropylation of toluene with acidic ionic liquids of the type $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$].

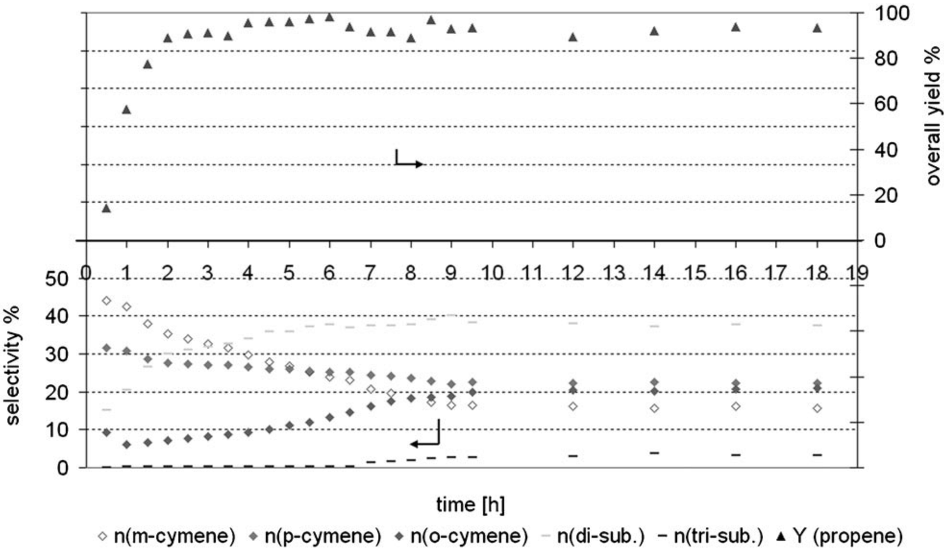

Figure 5. Continuous isopropylation of toluene in a liquid-liquid biphasic mode using the catalyst system $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] in a continuous loop reactor. *Conditions:* $T=50\,°C$; $p=40$ bar; mole flow $\dot{n}$(propene) = 8.7 mmol min^{-1}; mole flow $\dot{n}$(toluene) = 30 mmol min^{-1}; mole flow $\dot{n}$(cyclohexane) = 30 mmol min^{-1}; volume flow $\dot{V}$(circulation) = 3 L min^{-1}; residence time = 32 min; $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] = 2.5; m([BMIM][$CF_3SO_2)_2N$]/$AlCl_3$) = 45 g.

ene when the reaction was started). In addition, we wanted to investigate whether the observed change in selectivity with time over the first ten hours (in particular between 4 h and 10 h time on stream when the product yield is constantly high) could also be attributed to some Al leaching. Interestingly, after 8 h time on stream the system obviously stabilises with almost constant selectivities with the following 10 h.

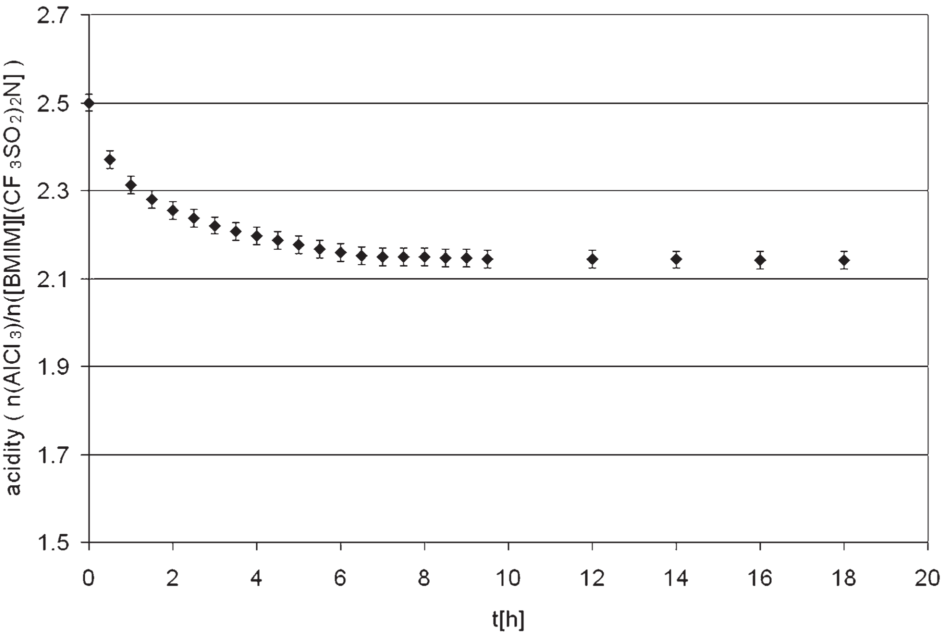

Figure 6. Al leaching from the ionic catalyst system during the long-term experiment as calculated from the results of ICP-AES analyses of the separated organic phases after different times-on-stream.

ICP-AES Analysis to Check for Al Leaching from the Catalyst System

Some Al leaching could be convincingly confirmed by accompanying ICP-AES analyses in which the Al contents of the isolated organic product phases were monitored over time-on-stream. The graph in Figure 6 has been calculated from these ICP-AES results by expressing Al leaching data as decreasing $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] ratio of the remaining ionic liquid catalyst phase.

The curve shows clearly that Al leaching is relatively significant in the first 8 h of the experiment while only negligible amounts of aluminium-containing compounds are lost into the organic phase between 8 h and 18 h time-on-stream. The latter fact is remarkable taking into account that in our experiment about 30 mL ionic liquid are extracted every hour of the experiment with more than 1 litre of organic phase. Thus between 8 h time-on-stream and 18 h time-on-stream the catalyst layer is extracted with about 10 litres organic reaction mixture with only negligible amounts of Al leaching detected in the ICP-AES analyses. This proves impressively the operational stability of our catalyst system $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] once a certain ratio of $AlCl_3$ to matrix ionic liquid [BMIM][$(CF_3SO_2)_2N$] and thus a certain ionic liquid acidity is reached. The change in leaching behaviour over reaction time is explained by the fact that the initial catalyst system $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$]$=2.5$ represents a complex mixture of acidic anionic species. Some of these anionic species may be relatively labile with a chance to release neutral molecules, such as, for example, Al[$(CF_3SO_2)_2N$]$_3$,[7] into the organic phase. Once these anions have degraded over time, the system stabilises, indicating the presence of very robust anionic, acidic species in the system at acidities around $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$]$=2.1$. As this ratio is still far above the minimum acidity of 1.5 which is required to catalyse the reaction (see Figure 2), the system remains highly active for the Friedel–Crafts reaction under investigation, however, with somewhat changed selectivity compared to the initial higher acidity.

It is quite illustrative to present the relative product distribution of the three monoalkylated products in a triangle diagram (Figure 7). The arrow in the Figure indicates the change in the ratio of the three cymene products over the first 8 h reaction time.

At the beginning of the alkylation reaction – where the high toluene to propene ratio largely determines the selectivity – the mixture of monoalkylated products happens to be near to the thermodynamic equilibrium. However, the stable catalytic system obtained after 8 h time-on-stream operates clearly under kinetic control. The ratio of the three cymene isomers realised for the subsequent 10 h time-on-stream was found to be 1:1.6:1.8 for *m*-cymene/*p*-cymene/*o*-cymene under our operation conditions.

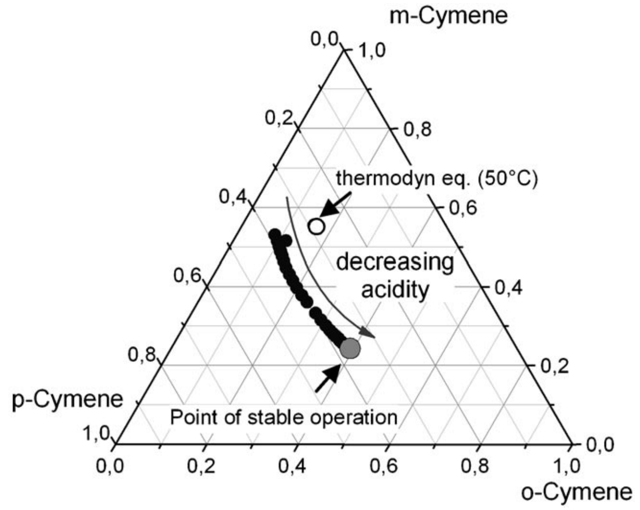

Figure 7. Product distribution of the monoalkylated products during the long-term experiment; the curved arrow indicates the change with time; the indicated value for the thermodynamic equilibrium is taken from ref.[16]

Conclusions

Our results show clearly that the immobilisation of Lewis acids in ionic liquids offers a new and very attractive method for continuous, liquid-liquid biphasic Friedel–Crafts alkylation reactions. The miscibility gap of the aromatic products with the catalyst phase combined with a significant density difference between catalyst phase and product mixture (*ca.* 0.6 g/mL) enable very effective product separation in the internal gravity separator of a loop reactor. The catalyst system $AlCl_3/[BMIM][(CF_3SO_2)_2N]=2.5$ was applied in a 18-h continuous run in which more than 18 litres of reaction mixture were processed in the reactor with yields greater than 90% with respect to the stoichiometric limiting component propene. The acidity of the catalyst system decreased in the first 8 h from 2.5 to 2.1 due to Al leaching into the organic phase. This change in acidity resulted in a pronounced change in selectivity to the different cymene products. Interestingly, the system stabilised at an $AlCl_3/[BMIM][(CF_3SO_2)_2N]$ ratio of 2.1 for the remaining 10 h of the experiments in which stable activity and stable selectivity could be demonstrated. Future work will deal with detailed kinetic studies of a slightly modified system under continuous operation as well as attempts to maximise the catalytic activity with respect to Al equivalents applied. In this way we would like to gain more insight into Lewis acid-catalysed, liquid-liquid biphasic, ionic liquid processes to further evaluate the technical applicability of such systems.

Experimental Section

General Remarks

All chemicals – except cyclohexane and toluene – were obtained from commercial sources (Fluka, Aldrich, Merck) and used without further purification. Cyclohexane and toluene (BASF) were dried using a solvent treatment rig from Glass Contour and stored under argon prior to use. All other chemicals were also stored under argon. The ionic liquid $[BMIM][(CF_3SO_2)_2N]$ was prepared and characterised according to well-known procedures[14] and dried overnight at 80 °C under high vacuum. Its water content was confirmed to be below 20 ppm prior to application by Karl–Fischer titration using a Metrohm 756 KF Coulometer with a Hydranal® Coulomat AG reagent. All synthetic reactions were performed in dried glassware under a static pressure of argon. Liquids and solutions were transferred with syringes.

GC analyses were carried out using a Varian CP 3900 FID. The analytical error has been checked to be below 2% relative to the measured values. Conditions: column: 50 m×0.25 mm CPSIL PONA CB $D_F=0.5$ μm; temperature profile: 110–250 °C, 15 iso, 15 °C min^{-1}, 15 min iso; injector temperature: 250 °C; eluent: H_2; volume flow: 1 mL min^{-1}.

All detected products were given in yields of *o*-, *m*- , *p*-cymene or grouped as di- or trisubstituted products. The combined yield of all indicated products and product fractions equals the overall product yield.

^{1}H and ^{13}C NMR spectra were recorded in DMSO on a Jeol 400 MHz spectrometer.

ICP-AES Analysis

ICP-AES analyses were performed using a Perkin–Elmer Emissions-Spectrometer Plasma 400. For sample preparation, the organic sample (~2 g) was two times extracted with 50 mL distilled water. The combined aqueous phases were then analytically investigated.

Preparation of the Catalyst

The calculated amount of $AlCl_3$ was added in portions slowly to the liquid $[BMIM][(CF_3SO_2)_2N]$ at room temperature under strictly inert conditions to avoid any effect of the atmospheric moisture. The flask was heated with an oil bath to 80 °C and the contents were vigorously stirred until the $AlCl_3$ was completely dissolved.

Batch Experiments

The alkylation reactions were carried out in 250-mL three-neck flasks, immersed in an oil bath with an automatic temperature controller. The flasks were equipped with a gas inlet, a reflux condenser and magnetic stirrer. The reactants were introduced into the flask under strictly inert conditions in order to avoid any effect of the atmospheric moisture. After the completion of the reaction, the organic layer containing the products and unreacted reactants was separated from the ionic liquids layer by decantation. The products were washed with water, dried over Na_2SO_4 and analysed by gas chromatography.

For the recycling experiments the ionic liquid was three times extracted with cyclohexane in order to remove all organic products. Afterwards the ionic liquid was re-injected into the flask and the experiment was repeated as described before.

Continuous Experiments[15]

The acidic ionic liquid, typically about 45 g of $AlCl_3$/[BMIM][$(CF_3SO_2)_2N$] = 2.5, was injected in the loop reactor that was completely evacuated for several hours and filled with inert gas (N_2). The aromatic compound (diluted with cyclohexane) was introduced first in the liquid phase by HPLC pump (toluene/cyclohexane: 0.4–40 $mL\,min^{-1}$) so that the reactor was totally filled with liquid. The reaction started with the liquid introduction of propene by HPLC pump (propene: 0.01–10 $mL\,min^{-1}$). A back-pressure regulator ensured a constant pressure (0–60 bar). The total volume of the continuous rig was determined to be 285 mL, showing 11% of short circuit flow and 31% of the flow not fully back-mixed (e.g. due to dead volume in the separator). Two static mixers (Sulzer SMX DN6) dispersed the ionic liquid with the organic reactants. A circulation pump (1–4.5 $L\,min^{-1}$) provided enough energy for a fine dispersion, while heat exchangers controlled the reaction temperature (15–95 °C). At the gravimetric phase separator, a diffuser absorbed out the kinetic energy of the dispersed liquids so that the ionic liquid settled down and were recirculated in the loop while a part of the organic products was discharged from the loop reactor.

Since the loop circulation flow was larger compared to the continuous inflow of feedstock and outflow of products, the system in use was characterised by a residence time distribution similar to a CSTR (continuous stirred tank reactor). Hence, the most part of the organic phase is being recirculated several times before leaving the reactor.

After a certain time a quantitative amount of the products was neutralised by washing with distilled water and analysed by gas chromatography.

In order to obtain the amount of alumina which was discharged from the reactor, the water from the neutralising process was analysed with a Perkin–Elmer Emissions Spectrometer Plasma 400. Since no ionic liquid was discharged from the loop reactor the remaining alumina and hence the remaining acidity of the ionic liquid in the reactor could be easily calculated.

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