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Selective dimerisation of 1-butene in biphasic mode using buffered chloroaluminate ionic liquid solvents — design and application of a continuous loop reactor

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Abstract

The dimerisation of 1-butene using (cod)Ni(hfacac) **1** as catalyst has been investigated in different chloroaluminate ionic liquids. Systems prepared by buffering an acidic ionic liquid with weak organic bases proved to be very suitable solvents for the reaction. The reaction takes place in biphasic reaction mode with facile catalyst separation and catalyst recycling. The high intrinsic dimer linearity of catalyst **1** is maintained, but with significant enhancement of catalyst activity and of the selectivity to the dimer product over that observed in toluene solvent. For further investigation, a continuous reactor was designed. Our results in continuous mode show the general technical applicability of the selective Ni-catalysed dimerisation in chloroaluminate ionic liquids using a loop reactor concept. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ionic liquids; Dimerisation; 1-Butene; Nickel; Loop reactor

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1. Introduction

Catalysis in liquid/liquid biphasic systems provides an attractive solution to the problem of separation of products from expensive transition metal catalysts. The reaction mixture consists of two immiscible solvents. Only one phase contains the catalyst allowing easy product separation by simple decantation. The catalyst phase can be recycled without any further treatment. Another attractive feature of biphasic catalysis is the possibility to extract intermediate products during the catalytic reaction into the organic layer. This often offers new possibilities to control the product selectivity. However, the right combination of catalyst, catalyst solvent and product is crucial for the success of biphasic catalysis [1].

Recently, a new approach has been adopted for biphasic catalysis, involving the use of catalyst solvents known as ionic liquids, which are simply salt mixtures of melting point below ambient. Ionic liquids form biphasic systems with many organic liquids such as, e.g. C_8-olefines. Moreover, their non-volatile character allows distillative product separation from the catalyst without the formation of azeotrops and without any solvent contamination of the product [2,3].

Well-studied examples for ionic liquids involve salt mixtures of aluminium halides in combination with suitable substituted organic cations such as, e.g. 1-ethyl-3-methylimidazolium (EMIM), 1-butyl-3-

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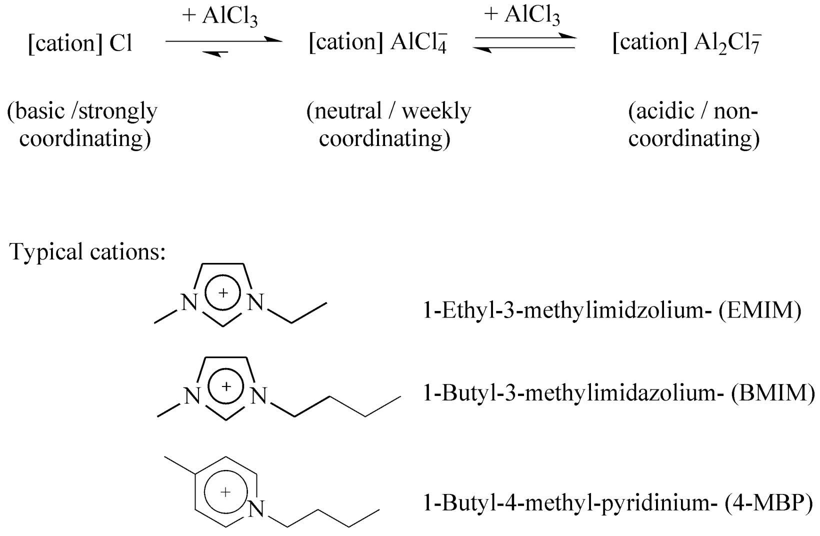
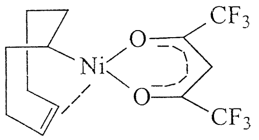


Fig. 1. Equilibria in chloroaluminate ionic liquids.

methylimidazolium (BMIM) or 1-butyl-4-methylpyridinium cations (4-MBP) [4–6] (Fig. 1).

The biphasic oligomerisation of olefins using chloroaluminate ionic liquids as catalyst solvent for Ni-complexes has been first described by Chauvin et al. [7–10]. These authors used a slightly acidic ionic liquid of the type [cation] $Cl/AlCl_3/AlEtCl_2$ as solvent for a Ni(II)-catalyst precursor. Dissolved in the chloroaluminate ionic liquid the Ni-catalyst showed significantly enhanced catalytic activity. After the reaction the ionic catalyst solution could be separated from the organic products by a simple decantation step allowing complete catalyst recovery. In the case of butene oligomerisation [9] using $[Ni(MeCN)_6]$ $[BF_4]_2$ as catalyst, the distribution of butene dimers (typically 39 ± 1% dimethylhexenes, 56 ± 2% monomethylheptenes and 6 ± 1% *n*-octenes) was reported to be independent of the addition of phosphine ligands. Moreover, the product mix was independent of feedstock, with both 1-butene and 2-butene yielding the same dimer distribution, with only 6% of the linear product.

To our knowledge, the best catalytic systems for producing linear dimers from 1-butene in conventional organic solvents originated from Keim et al. in 1979 [11], namely square planar Ni-complexes with O,O′-chelating ligands such as, e.g. (cod)Ni(hfacac) $\underline{\mathbf{1}}$.



$\underline{1}$

In toluene, e.g., $\underline{\mathbf{1}}$ is active in the dimerisation of 1-butene at a temperature >50°C, but reaches its maximum activity at 90°C with a turnover frequency of $500\,h^{-1}$. With an overall dimer selectivity of 85%, the selectivity to the linear dimer product is as high as 75%. Although the product quality produced by catalyst $\underline{\mathbf{1}}$ is of industrial interest, the combination of high ligand costs, low catalyst activity and difficult catalyst recovery from the homogenous reaction mixture, has prevented industrial development. Attempts to heterogenize $\underline{\mathbf{1}}$ on solid surfaces have been unsuccessful due to heavy leaching problems. The immobilisation of $\underline{\mathbf{1}}$ in a biphasic reaction system using water or butandiol as catalyst solvent resulted in complete deactivation of the catalyst.

In the present paper, we report the selective dimerisation of 1-butene in buffered chloroaluminate ionic liquids. First results were obtained in a 30 ml glass autoclave. To test the technical applicability of the developed catalytic systems, a continuous loop reactor was designed.

2. Results

2.1. Batch experiments

2.1.1. Use of buffered chloroaluminate ionic liquids as catalyst solvent

Generally, chloroaluminate ionic liquids are synthesised by mixing an organic chloride salt [cation] Cl with $AlCl_3$. The ratio of the two components is known to determine the chemical and physical properties of the resulting ionic liquid [12].

From former experiments, it was known that a selective Ni-catalysed dimerisation in chloroaluminate ionic liquid requires a slightly acidic environment [8,13]. This knowledge based on two observations. On the one hand, it was found that Ni-catalysts show no oligomerisation activity in basic chloroaluminate ionic liquids [$X(AlCl_3) < 50\,mol\%$] due to the presence of strongly coordinating chloride ions. On the other hand, acidic ionic liquids [$X(AlCl_3) > 50\,mol\%$] containing the anions $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ are known to initiate fast cationic oligomerisation which produce a large number of branched higher oligomers.

When we started our investigations, two different ways to produce slightly acidic ionic liquids were known from literature. The first uses alkalichlorides as buffering agents [14]. The second method includes the addition of alkylchloroaluminates to an acidic chloro-aluminate ionic liquids [7].

We used both procedures to synthesise slightly acidic ionic liquids for the oligomerisation of 1-butene with the Ni-catalyst **1**. The ionic catalyst solution was prepared by mixing the organic chloride salt with $AlCl_3$ according to the desired melt composition. **1** was dissolved in the resulting liquid. Additional alkali metal chloride or aluminiumalkyle were added afterwards. After the biphasic reaction according to Fig. 2, the remaining organic layer was hydrogenated for determination of the linearity of the dimer products (determination of products by GC–MS and comparison with authentic samples).

As shown in Table 1, first dimerisation experiments were carried out in ionic liquids buffered with LiCl. It is well-known that the addition of LiCl to an acidic chloroaluminate ionic liquid results in a dissolution of LiCl equivalent to the number of moles $Al_2Cl_7^-$ initially present and buffers the melt [15]. However, additionally added LiCl does not dissolve in the neutralised ionic liquid. The dimerisation was investigated in ionic liquids with and without solid alkali metal chloride present in the reaction system (Table 1, entries 1–3). Using buffered ionic liquids with solid LiCl present in the system we intended to study the effect of a "chloride storage" in the reaction system (Table 1, entry 1). Almost no Ni-catalysed dimerisation was observed. Obviously, the added electrophilic Ni-complex is "buffered" in the same way as the Lewis-acidic chloroaluminate species by the excess of solid alkali metal chloride. The resulting Ni-chloro-complexes were found to be non-reactive in the dimerisation of 1-butene.

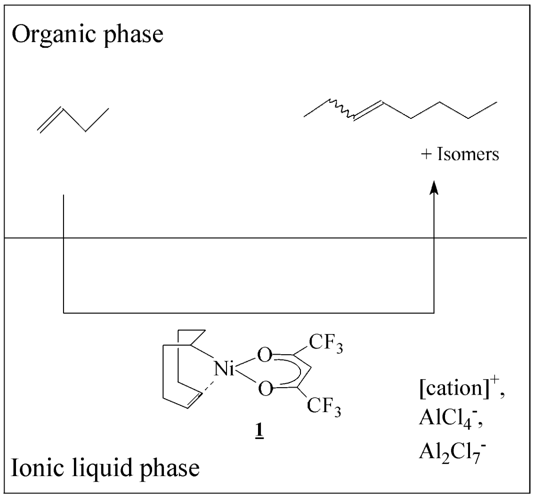


Fig. 2. Biphasic dimerisation of 1-butene using chloroaluminate ionic liquids as catalyst solvent.

In buffered ionic liquids without solid LiCl present, the extent of cationic side reaction was found to be dependent from the "latent acidity" of the melt. This term describes the known effect that even very weak bases (B:) form adducts with $AlCl_3$ in chloroaluminate ionic liquid that have been buffered to neutrality by alkali chloride addition [15,16]. The strenght of the "latent acidity" is known to be dependent from the $Al_2Cl_7^-$ content of the melt from which the buffered ionic liquid was prepared. Apparently, an additional driving force for the adduct formation results from the precipitation of solid alkalichloride: $AlCl_4^- + Li^+ + B : \rightleftharpoons B : AlCl_3 + LiCl\,(s)$. Our results indicate, that 1-butene can act as such a weak base. Therefore, it is not surprising that the extent of cationic side reaction

Table 1
Dimerisation of 1-butene with (cod)Ni(hfacac) $\underline{\mathbf{1}}$ in acidic ionic liquids buffered with LiCl and $AlEtCl_2$[a]

Entry	Ionic liquid system (mol% composition)	*T* (°C)	TOF (h^{-1})[b]	S(C_8) (%)[c]	L(C_8) (%)[d]
1	4-MBP Cl/$AlCl_3$ (0.45/0.55) buffered with excess LiCl[e]	25	[f]	–	–
2	4-MBP Cl/$AlCl_3$ (0.33/0.66) buffered with excess LiCl[g]	25	[h]	16	28
3	4-MBP Cl/$AlCl_3$ (0.45/0.55) buffered with excess LiCl[g]	25	7500	75	30
4	4-MBP Cl/$AlEtCl_2$ (0.36/0.64)	25	0[i]		
5	4-MBP Cl/$AlEtCl_2$ (0.36/0.64)	−10	61	96[j]	12
6	4-MBP Cl/$AlCl_3$/$AlEtCl_2$ (0.43/0.53/0.04)	25	415	73	37

[a] General conditions: 4 g ionic liquid, 0.04 g $\underline{\mathbf{1}}$, 12 g 1-butene; reaction time was varied in order to reach comparable conversions of 15–20%.

[b] Turnover frequency (TOF) in mol of butene converted per mol of nickel per hour.

[c] Selectivity to dimer product in %.

[d] Selectivity to linear dimer in the dimer fraction of the product in %.

[e] Ionic liquid was buffered with excess of dry LiCl (dried 14 days over P_2O_5 at 150°C). The ionic liquid used for reaction contained solid excess LiCl.

[f] Traces of cationic oligomers.

[g] Ionic liquid was buffered with excess of dry LiCl (dried 14 days over P_2O_5 at 150°C). Solid excess LiCl was filtered off. The ionic liquid used for reaction was a clear liquid and contained no solid excess LiCl.

[h] The product is mainly formed by a cationic oligomerisation mechanism of acidic species in the ionic liquid. The calculation of a turnover frequency related to the amount of nickel catalyst would be meaningless in this case.

[i] Catalyst decomposes and forms a black solid of elemental Ni.

[j] No product resulting from a parallel cationic side reaction is detected.

correlates well with the extent of "latent acidity" (comparison of entries 2 and 3 in Table 1).

The preparation of slightly acidic ionic liquids by addition of aluminiumalkyles to an acidic chloroaluminate ionic liquid and the use of these liquids as solvent for Ni-complexes has been studied extensively by Chauvin et al. [8]. However, we found that for the linear dimerisation of 1-butene with the Ni-complex $\underline{\mathbf{1}}$ these systems are not very suitable. High amount of aluminiumalkyles in the ionic liquid lead at room temperature to immediate catalyst decomposition (Table 1, entry 4). At −10°C, rapid decomposition could be avoided but the linearity of the dimer products was still low (Table 1, entry 5). Probably, even at this low temperature, $AlEtCl_2$ affects rapidly the Ni-X,Y-chelating system, which is known to be responsible for the linear selectivity of $\underline{\mathbf{1}}$. Furthermore, $AlEtCl_2$ is known to exhibit strong isomerisation activity [17] for converting 1-butene rapidly into the thermodynamic distribution of butenes (about 4% 1-butene at room-temperature). Due to the fact that only the terminal olefin can form linear dimers this influences significantly the linearity of the dimer product.

The linear selectivity was enhanced slightly using a mixed system of the form 4-MBP/$AlCl_3$/$AlEtCl_2$ but remained still unsatisfying low at 37% (Table 1, entry 6). Generally, the addition of aluminium alkyls limits the reaction temperature in order to avoid reduction of the Ni-catalyst. With respect to the exothermic nature of the dimerisation this may be a general concern for a technical application of dimerisation systems using ionic liquids with high amounts of aluminiumalkyles. For efficient heat utilisation it would be of interest to remove the dimerisation heat at a higher temperature level.

Taking these drawbacks into account, we decided to develop for our special application an alternative method to prepare slightly acidic ionic liquids. We found that an acidic chloroaluminate ionic liquid buffered with small amounts of weak organic bases provides a solvent which allows a selective, biphasic reaction using Ni-catalyst $\underline{\mathbf{1}}$. The function of the base is to trap any free acidic species in the melt which may initiate cationic side reactions (Table 2).

Table 2
Function of the added organic base B:

$$Al_2Cl_7^- + B : \rightleftharpoons B\text{–}AlCl_3 + AlCl_4^-$$
$$B\text{-}AlCl_3 + HCl \rightleftharpoons HB^+ + AlCl_4^-$$

$$Al_2Cl_7^- + HCl + B : \rightleftharpoons HB^+ + 2\,AlCl_4^-$$

Table 3
Linear dimerisation of 1-butene with (cod)Ni(hfacac) <u>**1**</u> in chloroaluminate ionic liquids buffered with different organic bases[a]

Entry	Base	TOF (h^{-1})[b]	S(C_8) (%)[c]	L(C_8) (%)[d]
1	Pyrrole	1350	86	56
2	*N*-methylpyrrole	2100	98	51
3	Chinoline	1240	98	64
4	Pyridine	550	78	33
5	2,6-Lutidine	2480	55	68
6	Di-*tert*-butylpyridine	2100	49	32
7	2,6-Dichloropyridine	56	34	74
8	2,6-Difluoropyridine	730	29	72

[a] General conditions: 4 g ionic liquid; composition of the ionic liquid: 4-MBP Cl/$AlCl_3$/base = 0.43/0.53/0.04; 0.04 g <u>**1**</u>, 12 g 1-butene; reaction time was varied in order to reach comparable conversions of 15–20%.

[b] Turnover frequency (TOF) in mol of butene converted per mol of nickel per hour.

[c] Selectivity to dimer product in %.

[d] Selectivity to linear dimer in the dimer fraction of the product in %.

Suitable bases have to fulfil a number of requirements. Its basicity has to be in a certain range in order to provide enough reactivity to eliminate all free acidic species in the melt. At the same time, it has to be non-coordinating with respect to the catalytic active Ni-centre. Another important feature is a very high solubility in the ionic liquid. During the reaction the base has to remain in the ionic catalyst layer even under the condition of intense extraction of the ionic liquid by the organic layer. Finally, the base has to be inert against the 1-butene feedstock and the oligomerisation products.

Table 4 shows the results of dimerisation experiments with catalyst <u>**1**</u> dissolved in acidic chloroaluminate ionic liquids buffered with different bases. The use of pyrrole and *N*-methylpyrrole was found to be particular successful (Table 3, entries 1 and 2). Specially by addition of *N*-methylpyrrole all cationic side reactions could be effectively suppressed and only dimerisation products produced by Ni-catalysis were obtained. In this case the dimer selectivity was as high as 98%. It is noteworthy that in contrast to, e.g. pyridine, *N*-methylpyrrole could be used even in higher concentrations without affecting the catalytic activity of the Ni-complex. This is explained by the fact that *N*-methylpyrrole cannot block the electrophilic Ni-centre by σ-bond formation.

The experiments with substituted pyridine derivatives as buffering base are interesting in two different respects (Table 3, entries 3–8): While the pyridine-buffered 1-butene oligomerisation shows a significantly lower activity, this is not the case for the alkyl-substituted pyridines. This is probably due to a stronger coordination of the unsubstituted pyridine to the active centre during reaction, in contrast to the sterically more demanding pyridine derivatives. Moreover, the S(C_8) selectivity clearly decreases with the steric demand of the *o*-substitution on the pyridine. Assuming that the S(C_8) can be regarded as an indicator of the efficiency of the buffering process, this is a clear sign for a considerable contribution of a sterically-demanding step in the buffering process. If only superacidic protons were responsible for the observed cationic side reaction in acidic ionic liquids, these should be perfectly buffered by a strong base like 2,6-di-*tert*-butylpyridin, which is not the case. It is assumed therefore that the reaction $Al_2Cl_7^- + \text{base} \rightleftharpoons AlCl_3\text{–base} + AlCl_4^-$ plays a major role in the buffering process. Halogen substitution in *o*-position of the pyridine reduces significantly the catalyst activity (Table 3, entries 7 and 8). Moreover, the low dimer selectivity observed in these cases indicates an influence of the electron withdrawing groups on the buffering ability of the base.

Table 4
Comparison of the linear dimerisation of 1-butene with (cod)Ni(hfacac) <u>**1**</u> in toluene and in a slightly acidic chloroaluminate ionic liquid

Reaction in toluene	Reaction in 4-MBP[a] Cl/$AlCl_3$/chinoline = 0.43/0.53/0.04
Monophasic	Biphasic, no detectable leaching[b]
No activity of the catalyst <50°C	High activity even at −10°C
Results (90°C): turnover frequency (TOF) = 500 h^{-1}, selectivity to dimer product: 85%, linearity = 75%	Results (25°C): turnover frequency (TOF) = 1240 h^{-1}, selectivity to dimer product: 98%, linearity = 64%

[a] 4-Methylbutylpyridinium.

[b] No nickel detected in the organic phase by X-ray fluorescence analysis.

2.1.2. Comparison with the monophasic reaction in toluene

Table 4 shows a comparison of the dimerisation of 1-butene with (cod)Ni(hfacac) **1** in chloroaluminate ionic liquids with the identical reaction carried out in toluene. Obviously, the variation of the solvent causes major changes in the reactivity of catalyst **1**. The reaction in the ionic liquid solvent is biphasic enabling easy catalyst separation and recycling. While **1** requires an activation temperature of 50°C in toluene, the reaction proceeds in the ionic liquid even at −10°C. This indicates that the catalyst activation, which is believed to be the formation of the active Ni-hydride complex, proceeds much more efficiently in the chloroaluminate solvent.

Furthermore, the product selectivities obtained in both solvents reveals a significant higher dimer selectivity in the biphasic case. This can be understood by considering the fact that the C_8-product is much less soluble in the ionic liquid than the butene feedstock (by about factor 4). During the reaction, a fast extraction of the C_8-product into the organic layer takes place thus preventing consecutive C_{12}-formation. The linear selectivity is high in both solvents, however somewhat lower in the ionic liquid solvent.

2.2. Design of a continuous flow reactor for the biphasic dimerisation of 1-butene

Encouraged by the promising results from the batch reactions we decided to scale up into a continuous flow reactor. Our aim was to prove the technical applicability of the biphasic catalytic reaction involving chloroaluminate ionic liquids and to study the stability of the ionic catalyst solution. With respect to the latter task we decided to immobilise the ionic catalyst solution over the whole reaction time in the reactor without any exchange or regeneration. Furthermore, the reactor design should allow a wide range of temperature (−10 to 100°C) and pressure (up to 100 bar) in order to study the effect of different dimerisation conditions on the product distribution. Additionally, the biphasic, exothermic character of the dimerisation reaction required intense mixing (to maximise the exchange surface) and a high ratio of heat exchange surface/reactor volume (for efficient heat removal). Finally, the reactor concept should minimise the reactor volume ($V_R < 300$ ml) in order to reduce the quantity of ionic catalyst solution necessary for the experiments.

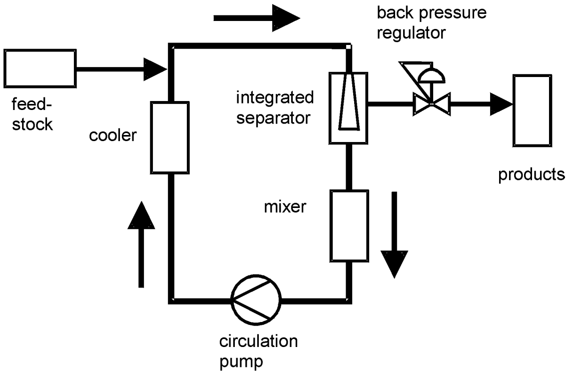


Fig. 3. Scheme of the loop reactor used for continuous dimerisation experiments.

All these requirements were fulfilled in the best way by a loop reactor concept as shown schematically in Fig. 3. The loop reactor used for our experiments had a volume of 160 ml. The biphasic reaction mixture was circulated by a circulation pump with high flow rates (4 l/min). Under these conditions, two static mixers in the reactor loop provided an efficient dispersion of the ionic catalyst solution in the organic phase. Two cooler/heater ensured full temperature control. Prior to the catalytic reaction, the ionic catalyst solution was placed into the reactor loop. During the reaction, the separation of the product from the ionic catalyst solution was realised with a gravity separator that was integrated in the reactor loop. Thus, in contrast to the use of an external separator, all catalyst was always present in the reactor. This allowed a direct observation of the catalyst's reactivity by analysis of the isolated products.

2.3. Catalytic experiments in continuous mode

For a typical dimerisation experiment in the continuous flow rig, **1** was dissolved in about 60 g slightly acidic ionic liquid. The reactor was filled with heptane and the biphasic mixture was circulated in the loop reactor. To start the reaction a mixture of heptane and 1-butene was fed into the reactor.

Table 5 shows the catalyst activity and product distribution after 60 min and after 176 min running

Table 5
Dimerisation of 1-butene with (cod)Ni(hfacac) **1** in buffered chloroaluminate ionic liquids using a continuous loop reactor[a]

Parameter/catalyst	Unit	**1**
Reaction condition		
Temperature	(°C)	40
Mass of ionic liquid	(g)	60.5
Feed	(g/min)	5.1
1-Butene in feed	(wt.%)	54
Heptane in feed	(wt.%)	46
Catalyst concentration	(mmol/l)	0.83
Catalyst activity and product distribution after 60 min		
TOF	(h^{-1})	1530
1-Butene	(% of C_4)	34
Trans-2-butene	(% of C_4)	45
Cis-2-butene	(% of C_4)	21
Linear octenes	(% of C_8)	58
Methylheptenes	(% of C_8)	40
Dimethylhexenes	(% of C_8)	2
Ratio C_8/C_{12}-product		98:2
Catalyst activity and product distribution after 176 min		
TOF	(h^{-1})	2700
1-Butene	(% of C_4)	42
Trans-2-butene	(% of C_4)	39
Cis-2-butene	(% of C_4)	19
Linear octenes	(% of C_8)	52
Methylheptenes	(% of C_8)	45
Dimethylhexenes	(% of C_8)	3
Ratio C_8/C_{12}-product		98:2

[a] **1**: (H-COD)Ni(hfacac); composition of the buffered ionic liquid: BMIM $Cl/AlCl_3/N$-methylpyrrole = (0.43/0.53/0.04).

time in the continuous loop reactor. Remarkably, both results are in good agreement with the results from the corresponding batch experiment (Table 3, entry 2).

This proves the general applicability of the loop reactor concept for a biphasic dimerisation in chloroaluminate ionic liquids. Obviously, the reactivity of the ionic catalyst solution is largely maintained over the 3 h reaction time. The slightly decreasing linear selectivity over time may be attributed to a slow abstraction of the hfacac-ligand from the Ni-centre during the reaction. However, the selectivity of the oligomerisation reaction to the dimer product remains very high even after 176 min (ratio C_8/C_{12}-product = 98:2). By further prolongation of the reaction time, an overall *turnovernumber* of catalyst **1** of more than 18 000 could be realised in the loop reactor.

3. Summary

A number of different chloroaluminate ionic liquids have been tested as solvents for the selective dimerisation of 1-butene using (cod)Ni(hfacac) **1** as catalyst. Those systems prepared by buffering an acidic ionic liquid with weak organic bases turned out to be the most suitable solvents for the reaction. Moreover, the buffering procedures reported here facilitate the use of an ionic liquid solvent for catalyst **1**, permitting reaction to take place in biphasic reaction mode with facile catalyst separation and catalyst recycling. The high intrinsic dimer linearity of catalyst **1** is maintained, but with significant enhancement of catalyst activity over that observed in toluene solvent. The selectivity to dimer product is significantly higher in the biphasic case using the ionic catalyst solvent. This is explained by a fast extraction of the C_8-product out of the catalyst layer thus preventing consecutive trimer formation.

To generate data of technical relevancy, a continuous reactor was designed. A loop reactor concept was found to be most suitable for testing the reactivity of **1** in continuous reaction mode. After 3 h reaction time the catalytic system under investigation showed still technically very attractive activity (TOF = 2700 h^{-1}) and selectivity (selectivity to C_8-product >98%, selectivity to linear C_8-product 52%).

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