

Ionic liquids—weakly-coordinating solvents for the biphasic ethylene oligomerization to α -olefins using cationic Ni-complexes

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Abstract

Hexafluorophosphate ionic liquids have been applied as catalyst phase in the selective, biphasic oligomerization of ethylene to 1-olefins with the cationic Ni-complex (η^3 -methallyl)[bis(diphenylphosphino)methane-monoxide- κ^2 -P,O]nickel(II) hexafluoroantimonate [(mall)Ni(dppmO)][SbF₆]. The biphasic reaction mode opens up the possibility for effective catalyst recycling and offers additionally an interesting way to enhance catalytic activity. Moreover, a remarkable influence of the biphasic reaction mode—which is enabled for the first time using the ionic liquid catalyst phase—on the product selectivity is observed. Interestingly, slight modifications of the ionic liquid's cation give access to a further tuning of the product distribution. Moreover, the results of our efforts to optimize the reactor design for the specific needs of this biphasic reactions and some recycling experiments are presented.

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1. Introduction

Higher α -olefins (HAOs) represent an important group of industrial chemicals which find a variety of end uses. Depending on their chain length, they are components of plastics (C₄–C₆ HAOs in copolymerisation), plasticizers (C₆–C₁₀ HAOs through hydroformylation), lubricants (C₁₀–C₁₂ HAOs through oligomerization) and surfactants (C₁₂–C₁₆ HAOs through arylation/sulphonation). HAOs can be obtained from ethylene via oligomerization processes, such as those practiced by BP Amoco (alkylaluminium catalyst) and Shell (SHOP, neutral nickel/phosphine catalyst). The latter is carried out as a biphasic process. While the catalyst is dissolved in 1,4-butanediol, the products form a second layer and are easily removed by simple phase separation. This reaction mode contributes significantly to the overall process economics [1,2].

Besides the neutral nickel/phosphine compounds used in the Shell Higher Olefins Process, cationic Ni-complexes have attracted some attention as highly active catalyst for

ethylene oligomerization. Due to their positive charge, they usually possess higher electrophilicity of the nickel center which often results in a higher oligomerization activity of the system [3–8].

Cationic Ni-complexes with P \wedge O-ligands such as (η^3 -methallyl)-[bis(diphenylphosphino)methane-monoxide- κ^2 -P,O]nickel(II) hexafluoroantimonate [(mall)-Ni(dppmO)][SbF₆] (see Fig. 1) proved to be especially suitable catalysts to oligomerize ethylene to α -olefins in high selectivity [3,9].

The results of the ethylene oligomerization with catalyst [(mall)Ni(dppmO)][SbF₆] in different organic solvents are presented in Table 1 [9].

While [(mall)Ni(dppmO)][SbF₆] shows good solubility in CH₂Cl₂ and CHCl₃, the complex does not dissolve in chlorobenzene. In CHCl₃ fast decomposition is observed. CH₂Cl₂ turned out to be the most suitable organic solvent for ethylene oligomerization with catalyst [(mall)Ni(dppmO)][SbF₆] (Table 1, entry a). In contrast, catalytic activity of the cationic Ni-complex in acetone and THF was found to be surprisingly low (Table 1, entries b and c). Obviously, these two more nucleophilic solvents already compete with ethylene for the coordination sites at the highly electrophilic Ni-center. Consequently, the catalytic activity in these solvents turns down since a significant part of the active catalytic species is blocked by the applied

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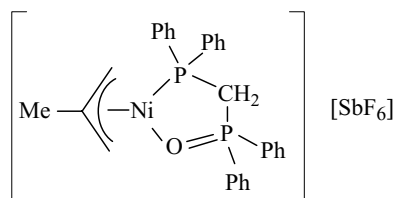


Fig. 1. The cationic Ni-complex $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$.

solvent. Furthermore, oligomerization of ethylene with catalyst $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ in *n*-pentane and toluene reveals remarkable results. These two solvents should show no ability to stabilize the polar transition state of the ionic Ni-complex due to their low dielectric constant. However, $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ shows still moderate activity in these solvents (Table 1, entries d and e).

While all organic solvents described so far form a monophasic reaction mixture with the products of the ethylene oligomerization, 1,4-butanediol is known to have a miscibility gap with higher α -olefins. Therefore, first experiments to carry out a biphasic ethylene oligomerization with catalyst $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ used this solvent as polar catalyst phase. However, in contrast to the industrially practiced SHOP, the cationic Ni-complex is almost completely deactivated by this solvent. This difference is another indication for the much higher electrophilicity of the cationic complex $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ in comparison to neutral Ni-complexes such as those used in the SHOP.

In fact, the results of all these experiments indicate that ethylene oligomerization with $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ requires a polar solvent (in order to dissolve the cationic Ni-complex) with low nucleophilicity (to avoid catalyst poisoning by the solvent). Even more difficult, the desired biphasic catalysis with the cationic Ni-catalyst affords a solvent with enough polarity to form a miscibility gap with the oligomerization products without affecting the catalytic center.

In the present paper we report about recent investigations from our laboratories dealing with the use of hexafluorophosphate ionic liquids as solvents for the biphasic

Table 1
Ethylene oligomerization with $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ in different organic solvents

Solvent	Activity (mol/mol)	Linearity ^a (%)	1-Olefin share ^b (%)	C_{max} ^c
CH ₂ Cl ₂	1692	87.1	64.4	16
Acetone	102	96.7	94.1	12
THF	<10	(a)	(a)	4
<i>n</i> -Pentane	540	59.5	47.1	12
Toluene	197	81.8	62.6	14
1,4-Butandiol	<10	(a)	(a)	4

0.1 mmol $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$; $t = 2$ h; 20 ml solvent; $T = 50$ °C; $p(\text{ethylene}) = 30$ bar; (a) low product formation prevents exact analysis.

^a Share of linear products in the C₆-fraction.

^b Share of 1-hexene in the linear C₆-products.

^c Maximum chain length of the formed oligomers.

oligomerization of ethylene using $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ as catalyst. The here described results expand on previously published, preliminary work by our group and Gordon et al. that had its focus mainly on the role of the ionic liquid as polar but weakly coordinating solvent [10].

Ionic liquids are simply salt mixtures of low melting points (<100 °C). They form biphasic systems with many organic liquids such as e.g. α -olefins. Moreover, their non-volatile character allows distillative product separation from the catalyst without the formation of azeotrops and without solvent contamination of the product [11].

Prior to the here described investigations (and their preliminary publication), most Ni-catalyzed oligomerization reactions in ionic liquids have been carried out in chloroaluminate systems. As early as 1990, Chauvin et al. published the first dimerization of propene in ionic liquids of the type 1-*n*-butyl-3-methylimidazolium([BMIM])Cl/AlCl₃/AlEtCl₂ [12]. Similar systems have been later used for the dimerization of 1-butene [13] and butenes mixtures [14,15] as well as for the oligomerization of ethylene [16].

The Ni-catalyzed oligomerization of ethylene in these systems was found to be characterized by high oligomerization and high isomerization activity. The latter leads to a rapid consecutive transformation of the formed α -olefins into mixtures of much less valuable internal olefins [16]. For this reason a highly selective ethylene oligomerization to α -olefins in chloroaluminate systems has not been observed to date.

2. Results and discussion

2.1. Screening experiments—Ni-catalyzed oligomerization in hexafluorophosphate ionic liquids

Imidazolium hexafluorophosphate ionic liquids act as inert solvents in many reactions (if carbene formation from the imidazolium cation and hydrolysis of the anion is avoided). In this case, the ionic liquid provides a polar, weakly coordinating medium for the transition metal catalyst.

Our first experiments aimed to answer the general question whether cationic Ni-complexes show any oligomerization activity in non-chloroaluminate ionic liquids. Therefore, we investigated the ethylene oligomerization with $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ in [BMIM][PF₆].

The catalytic systems were prepared by mixing $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ with the hexafluorophosphate ionic liquid at room temperature. [BMIM][PF₆] was prepared by reacting the chloride salt (purchased from Solvent Innovation GmbH, Cologne [17]; see literature [18] for the synthesis) with HPF₆ after a method described by Fuller et al. [19].

A first set of qualitative experiments revealed some very interesting results, however reproducibility was very poor. Obviously, the reaction is extremely sensitive to minor changes in the experimental protocol. In the following investigations, we learned that two aspects are of major influence and must therefore kept constant to obtain reproducible

results. (a) The content of halide ions in the hexafluorophosphate ionic liquid (from the alkylation step); (b) the content of water in the hexafluorophosphate melt (from the acidic exchange reaction). Since water and halide ions are known to poison the catalyst $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ [9] these two substances must be removed completely from the ionic liquid to allow maximum catalytic activity of the cationic Ni-complex. Additionally, even small amounts of water can lead to some hydrolysis of the hexafluorophosphate anion which would liberate traces of HF which also act as a poison to the cationic Ni-complex.

Optimization of the reported ionic liquid synthesis protocol revealed that an halide free ionic liquid can be obtained by washing the crude $[\text{BMIM}][\text{PF}_6]$ several times with water. The desired quality of the ionic liquid with respect to the halide content was obtained if the washing water gave no precipitation of AgCl after addition of AgNO_3 . The water was then removed by evacuation (10^{-5} bar) at 80°C over 24 h. Using this procedure for the synthesis of $[\text{BMIM}][\text{PF}_6]$, we were able to obtain fully reproducible oligomerization results with catalyst $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ dissolved in different batches of the ionic liquid $[\text{BMIM}][\text{PF}_6]$.

Furthermore, it was found in the first experiments that catalytic results are highly dependent on all modifications that influence mass transfer of ethylene into the ionic catalyst layer (type of reactor, type of stirrer, stirring rate). For a further, quantitative investigation of these effects we decided to carry out the oligomerization experiments in two different, well-defined autoclaves. A 75 ml autoclave (reactor 1, Fig. 2) with magnetic stirring bar (length 3.5 cm, diameter 0.4 cm) and a 150 ml autoclave with stirring from the top (reactor 2, Fig. 2). The latter was equipped with baffles to improve mixing of the two liquid phases.

Different types of stirrer were tested for the 150 ml autoclave. The design displayed in Fig. 3 proved to be the most suitable one to maximize ethylene transfer into the ionic liquid catalyst layer.

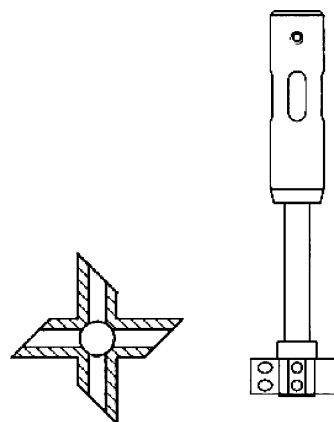


Fig. 3. Stirrer design to maximize ethylene transfer into the ionic liquid catalyst layer as used for oligomerization experiments in the 150 ml autoclave.

2.2. Comparison of ethylene oligomerisation with $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ in CH_2Cl_2 and in $[\text{BMIM}][\text{PF}_6]$

First quantitative experiments aimed to compare the reactivity of $[(\text{mall})\text{Ni}(\text{dppmo})][\text{SbF}_6]$ in the ionic liquid $[\text{BMIM}][\text{PF}_6]$ (biphasic system) with the results obtained in CH_2Cl_2 (monophasic reaction). In order to quantify the influence of different types of reactors and stirring, the comparison experiments were carried out in both reactors 1 and 2. The ethylene oligomerisation results are presented in Table 2.

In both solvents, CH_2Cl_2 and $[\text{BMIM}][\text{PF}_6]$, the ethylene conversion increases drastically in the 150 ml reactor. Obviously, even for the reaction in CH_2Cl_2 the ethylene availability at the catalytic Ni-center is still a limiting factor in the 75 ml autoclave. However, the rate enhancement observed in the case of $[\text{BMIM}][\text{PF}_6]$ being the catalyst solvent is clearly more significant (factor 4.3 ($[\text{BMIM}][\text{PF}_6]$) versus factor 2.0 (CH_2Cl_2)). This result is not surprising taking into

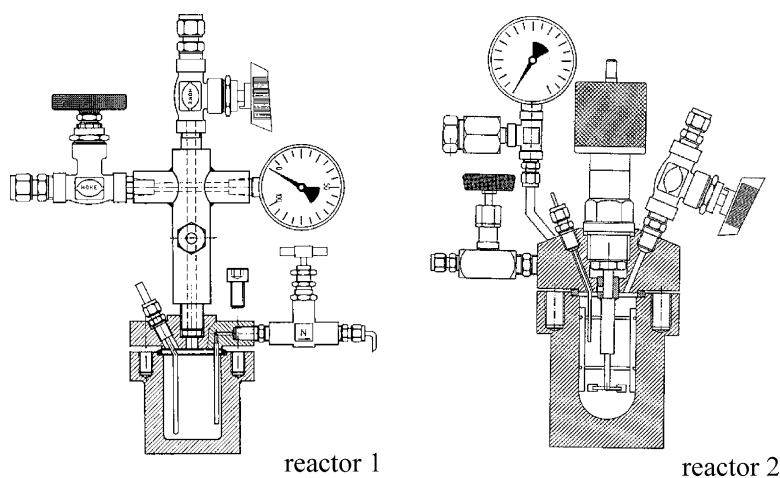


Fig. 2. Different types of reactors as used for the ethylene oligomerization experiments.

Table 2

Ethylene oligomerization with catalyst [(mall)Ni(dppmO)][SbF₆][−]—comparison of the reaction in CH₂Cl₂ and in [BMIM][PF₆]

Solvent	Reaction mode	Reactor ^a	Activity (mol/mol)	Linearity ^b (%)	1-Olefin share ^c (%)	α -value ^d	C _{max} ^e
CH ₂ Cl ₂	Monophasic	1	3,704	95.3	88.4	0.48	18
CH ₂ Cl ₂	Monophasic	2	7,591	94.3	90.1	0.43	18
[BMIM][PF ₆]	Biphasic	1	5,967	96.1	95.0	0.13	12
[BMIM][PF ₆]	Biphasic	2	25,425	94.9	93.2	0.16	14

0.05 mmol [(mall)Ni(dppmO)][SbF₆]; $t = 2$ h; p (ethylene) = 50 bar; $T = 25$ °C; 10 ml solvent; 20 ml heptane.^a Type of reactor used: 1, 75 ml autoclave with magnetic stirrer (stirrer length, 3.5 cm; diameter, 0.4 cm); 2, 150 ml autoclave with stirring from the top, baffles, and optimized design for maximum gas dispersion in the ionic liquid phase.^b Share of linear products in the C₆-fraction.^c Share of 1-hexene in the linear C₆-products.^d α -value of the oligomer distribution calculated as α in mol [Σ (C₁₀–Produkte)]/mol [Σ (C₈–Produkte)].^e Maximum chain length of the formed oligomers.

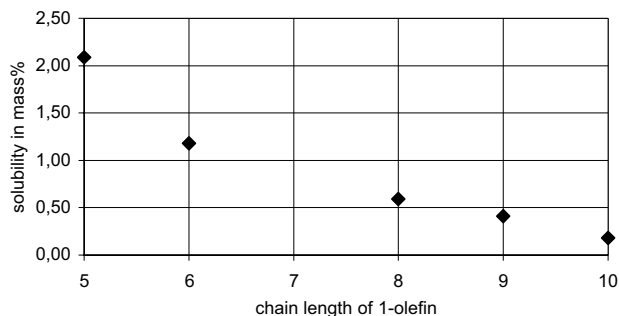
account that in the case of two liquid phases there is an additional transport barrier to bring enough ethylene into the catalytic active layer.

The comparison of catalytic experiments carried out in the same reactor reveals that catalyst [(mall)Ni(dppmO)][SbF₆] is clearly more active in [BMIM][PF₆] in comparison to CH₂Cl₂ under identical conditions. It is noteworthy, that the observed activation is definitely not caused by a loss of the catalyst's ligand as proved by the excellent selectivity for 1-olefins still obtained in the ionic liquid solvent. The selectivity in [BMIM][PF₆] is even slightly higher than in CH₂Cl₂. Overall 1-hexene selectivity in C₆-fraction (which reflects the product of "linearity" and "1-olefin share") is 84.2% in CH₂Cl₂ versus 91.3% in [BMIM][PF₆] (reactor 1) and 85.0% in CH₂Cl₂ versus 88.5% in [BMIM][PF₆] (reactor 2).

Interestingly, less internal hexenes (formed by consecutive isomerization of 1-olefins) are obtained in the case of biphasic oligomerization using the ionic liquid solvent.

This is explained by the much lower solubility of the oligomerization products in the catalyst solvent [BMIM][PF₆]. Since the formed 1-olefins are quickly extracted into the organic layer, consecutive isomerization of these products at the Ni-center is suppressed in comparison to the monophasic reaction in CH₂Cl₂. The solubility of some 1-olefins in [BMIM][PF₆] is shown in Fig. 4 [20].

Another interesting aspect in the comparison between the ethylene oligomerization with catalyst [(mall)Ni(dppmO)]-[SbF₆][−] in [BMIM][PF₆] and CH₂Cl₂ is the different

Fig. 4. 1-olefin solubility in [BMIM][PF₆] at 25 °C.

oligomer distribution obtained. The reaction in the ionic liquid shows a significantly shorter product distribution (see Fig. 5).

To understand this behavior, the ethylene solubility in the different solvents under reaction condition were measured using a method described by Mecking et al. [21]. While 6.51 g of ethylene dissolve in 10 ml CH₂Cl₂ at 25 °C/50 bar, the ethylene solubility in [BMIM][PF₆] under identical conditions is only 1.1 g. Since the rate of ethylene insertion is dependent from the ethylene concentration at the catalyst, but the rate of β -H-elimination is not, it becomes understandable that a low ethylene availability at the catalytic active center favors the formation of a shorter oligomer distribution.

However, ethylene solubility may not be the only reason to explain the different oligomer distribution found with [BMIM][PF₆] and CH₂Cl₂. Lower solubility of the growing Ni-alkyl-complex in the ionic liquid may be another aspect. We speculate that the catalytic active cationic Ni-complex gains more and more tensidic character while the alkyl chain is growing. The complex reaches the phase boundary where β -H-elimination should be enhanced for entropic reasons.

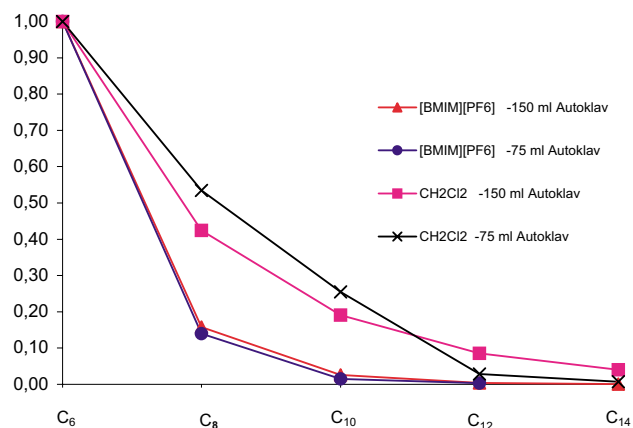


Fig. 5. Oligomer distribution in CH₂Cl₂ and [BMIM][PF₆]; experiments in reactors 1 and 2. Oligomer distribution obtained in the ethylene oligomerization with catalyst [(mall)Ni(dppmO)][SbF₆][−] in different hexafluorophosphate ionic liquids of general type [RMIM][PF₆].

Table 3

Biphasic ethylene oligomerization using [(mall)Ni(dppmO)][SbF₆] in hexafluorophosphate ionic liquids—cation variation

Solvent	Reaction mode	Activity (mol/mol)	Linearity (%)	1-Olefin share ^a (%)	α-value	C _{max}
[BMIM][PF ₆]	Biphasic	25,425	94.9	93.2	0.16	14
[HMIM][PF ₆]	Biphasic	11,154	91.4	89.7	0.18	14
[OMIM][PF ₆]	Biphasic	5,770	92.5	90.3	0.22	14
[DMIM][PF ₆]	Biphasic	4,016	96.2	94.9	0.24	16

150 ml autoclave (reactor 2); 0.1 mmol [(mall)Ni(dppmO)] SbF₆; *t* = 2 h; *p*(ethylene) = 50 bar; *T* = 25 °C; 20 ml heptane; 10 ml ionic liquid.^a In C₆-products. [BMIM], 1-*n*-butyl-3-methylimidazolium; [HMIM], 1-*n*-hexyl-3-methylimidazolium; [OMIM], 1-methyl-3-*n*-octylimidazolium; [DMIM], 1-*n*-decyl-3-methylimidazolium.

In Fig. 5 the different oligomer distributions in [BMIM][PF₆] and CH₂Cl₂ are shown. For easier comparison, the relative distributions are presented with the amount of C₆-product being set to 1.

2.3. Variation of the ionic liquid's cation

In another set of oligomerization experiments a systematic variation of the ionic liquid's cation was carried out. For better comparison only hexafluorophosphate ionic liquids with 1-*n*-alkyl-3-methylimidazolium ions were used (Table 3).

Although the solubility of the oligomerization products in the ionic liquid increases gradually with increasing chain length of the ionic liquid's cation, a biphasic oligomerization reaction takes place with all ionic liquids under investigation. The selectivity to 1-olefins shows no clear dependence on the ionic liquid's cation. However, oligomerization activity and oligomer distribution follow a clear tendency and require further explanation.

Obviously, the catalytic activity of [(mall)Ni(dppmO)][SbF₆] decreases with increasing alkyl chain of the ionic liquid's cation. At the first view, this behavior seems to be even more surprising, since the solubility of ethylene in the different ionic liquids increases with increasing chain length of the alkyl group at the ionic liquid's cation (Table 4).

However, the reduced activity in e.g. 1-*n*-decyl-3-methylimidazolium hexafluorophosphate ([DMIM][PF₆]) versus [BMIM][PF₆] becomes understandable taking into account the known fact, that the oligomerization activity of cationic Ni-complexes is generally reduced by the presence of internal higher olefins. Those are formed during the oligomerization to a small extend as by-products. In the case of the [BMIM][PF₆], rapid extraction of these by-products into

the product phase can be expected due to the low solubility for higher olefins. In the case of [DMIM][PF₆], a significant higher concentration of these by-products will build up in the catalyst phase and will reduce the catalyst's activity to some extent. Consequently, a higher solubility of oligomerization and isomerization products in the catalyst solvent results in lower catalytic activity of the cationic Ni-complex. Having this in mind, both, the enhanced activity of [(mall)Ni(dppmO)][SbF₆] in the biphasic system versus monophasic reaction in CH₂Cl₂ and the reduced activity in ionic liquids e.g. [DMIM][PF₆] versus [BMIM][PF₆] can be explained.

Finally, an interesting shift of the oligomer distribution is observed with the ionic liquid's cation carrying longer alkyl chains. In Fig. 6 the different oligomer distributions are presented as obtained in the ethylene oligomerization with [(mall)Ni(dppmO)][SbF₆] in the different hexafluorophosphate ionic liquids. Again, the relative distributions are presented with the amount of C₆-product being set to 1 to allow an easier comparison.

With increasing alkyl chain length at the ionic liquid's cation the oligomer distribution obtained becomes gradually broader. However, all biphasic oligomerization experiments still show much shorter oligomer distributions than in the case of the monophasic reaction in CH₂Cl₂ (under identical conditions).

Table 4

Solubility of ethylene in different solvents

Solvent	Solubility (g(ethylene)/10 ml solvent)
CH ₂ Cl ₂	6.51
[BMIM][PF ₆]	1.10
[HMIM][PF ₆]	1.25
[OMIM][PF ₆]	1.83

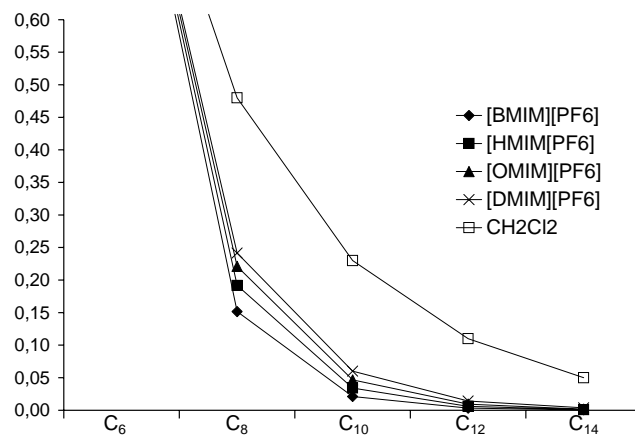
25 °C; *p*(ethylene) = 50 bar; [BMIM], 1-*n*-butyl-3-methylimidazolium; [HMIM], 1-*n*-hexyl-3-methylimidazolium; [OMIM], 1-methyl-3-*n*-octylimidazolium.

Fig. 6. Oligomer distribution obtained in the ethylene oligomerization with catalyst [(mall)Ni(dppmO)][SbF₆] in different hexafluorophosphate ionic liquids of general type [RMIM][PF₆].

Table 5
Recycling experiments

Cycle no.	Activity (mol/mol)	Linearity (%)	1-Olefin share ^a (%)	α -value	C_{\max}
1	25,424	95.1	93.2	0.16	14
2	19,778	94.1	92.8	0.16	14
3	15,904	93.8	91.7	0.16	14
Σ	61,106				

150 ml autoclave (reactor 2); 0.05 mmol [mall Ni(dppmO)][SbF₆]; $t = 2$ h; $p(\text{ethylene}) = 50$ bar; $T = 25$ °C; 20 ml heptane; 10 ml [BMIM][PF₆].

^a In C₆-products.

To understand the influence of the ionic liquid's cation on the oligomer distribution three aspects have to be taken into account: (a) higher ethylene solubility in ionic liquids with longer alkyl chain substitution at the cation (see Table 4); (b) higher solubility of the growing Ni-alkyl-complex in ionic liquids with longer alkyl chain substitution at the cation; (c) higher solubility of the already formed oligomers in ionic liquids with longer alkyl chain substitution at the cation. All three aspects favor chain growth or reinsertion of already formed oligomers and thereby shift the oligomer distribution to higher oligomers.

2.4. Recycling experiments

Since the use of hexafluorophosphate ionic liquids allowed for the first time a biphasic ethylene oligomerization with catalyst [(mall)Ni(dppmO)][SbF₆], practical questions such as catalyst recovery and the possibility for repetitive use of the isolated ionic catalyst solution attracted our interest. In Table 5 some typical results of our recycling experiments are presented.

The results confirm the general possibility of catalyst recycling. However, a more detailed evaluation of the obtained data is difficult at this stage since it was not possible to ensure completely inert condition for the ionic catalyst solution during the practical recycling process (phase separation, refill etc.). With regards to the extreme water sensitivity of complex [(mall)Ni(dppmO)][SbF₆] and the known hygroscopicity of the ionic liquid it is very likely that the observed drop in catalytic activity is caused by these handling problems. To confirm this hypothesis, we are actually about to build up a reactor system that allow a recycling of the ionic catalyst solution under completely inert conditions.

3. Conclusions

We could demonstrate that the use of hexafluorophosphate ionic liquids allows a selective, biphasic oligomerization of ethylene to 1-olefins with the cationic Ni-complex [(mall)Ni(dppmO)][SbF₆]. Obviously, the ionic liquid's ability to dissolve the ionic catalyst complex combined with a low solvent nucleophilicity accounts for the observed reactivity and phase behavior. Moreover, the possibility

to carry out the reaction in biphasic mode opens up new possibilities to improve catalytic activity, selectivity and to enhance catalyst lifetime.

The higher activity of [(mall)Ni(dppmO)][SbF₆] in e.g. [BMIM][PF₆] is explained by its weakly coordinating character and by the fast extraction of products and side products out of the catalyst layer into the organic phase. A high concentration of internal olefins (from oligomerization and consecutive isomerization) at the catalyst is known to reduce catalytic activity due to the formation of quite stable Ni-olefin complexes.

Selectivity of the ethylene oligomerization reaction is clearly influenced by the biphasic reaction mode. Oligomer distribution is found to be much shorter in the biphasic system due to restricted ethylene availability at the catalytic Ni-center in the ionic liquid. Fast oligomerization kinetics, relatively low ethylene solubility in the ionic liquid and limited mass transfer of ethylene into the ionic catalyst solution account for this behavior.

Finally, we could show that the ionic catalyst solution can be principally recycled. By repetitive use of the ionic catalyst solution the overall activity per mole catalyst can be increased dramatically.

Even if some practical questions (mainly concerning the recycling) are still to be answered in our ongoing research, we think that our studies could demonstrate the potential of hexafluorophosphate ionic liquids in a technical relevant oligomerization reaction. In this context it is noteworthy that the main disadvantage of using hexafluorophosphate ionic liquids, namely their (slight but clearly existent) sensitivity versus hydrolysis, is not a major drawback for the further development of the here described application. The catalyst complex [(mall)Ni(dppmO)][SbF₆] used in these investigations is highly sensitive versus hydrolysis anyway and very dry ethylene is usually available at petrochemical sites. Therefore, we hope that our investigations will help to bring biphasic ethylene oligomerization with cationic Ni-complexes closer to industrial reality.

4. Experimental section

4.1. General remarks

The synthesis of [(mall)Ni(dppmO)][SbF₆] was carried out under argon atmosphere using standard Schlenk techniques. All ionic liquids and the cationic Ni-catalyst were dried under *vacuo* and stored in a glove-box MB 150 B-G (Braun, H₂O and O₂ always <3 ppm). Ethylene was used as purchased from Linde AG (99.5% purity).

4.2. Synthesis of [(mall)Ni(dppmO)][SbF₆]

The synthesis of [(mall)Ni(dppmO)][SbF₆] was carried out following a procedure described by Keim and co-workers [9,22].

To a chilled suspension of $[(\eta^3\text{-methylallyl})\text{NiBr}]_2$ in 10 ml of dichloromethane at -20°C a solution of the biphosphine monoxide in 5 ml of the same solvent was added. The resulting red–brown suspension was stirred for an additional 30 min. After addition of a solution of silver hexafluoroantimonate in 5 ml dichloromethane the precipitating silver bromide was rapidly filtered off through Celite® after 5 min. The clear yellow filtrate was collected at -20°C . After several washings of the filter cake with 2 ml aliquots of dichloromethane the solvent was removed in vacuo giving yellow powders that were washed with diethyl ether and *n*-pentane. After drying in vacuo the complexes were obtained in analytically pure form.

Yield: 83%; *Anal. Calc.* for $\text{C}_{29}\text{H}_{29}\text{F}_6\text{NiOP}_2\text{Sb}\cdot\text{O}\cdot\text{5CH}_2\text{-Cl}_2$ (792.43): C, 44.71; H, 3.82. found: C, 44.54; H, 3.76. $^1\text{H NMR}$ (CD_2Cl_2 , 300 MHz, 293 K): [ppm] $\delta = 1.86$ (br s, 1H, H^1), 2.19 (s, 3H, Me), 2.60 (br s, 1H, H^2), 3.36 (m, 2H, CH_2), 3.48 (m, 1H, H^3), 4.47 (s, 1H, H^4), 6.50–8.50 (m, 20H, H_{arom}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz, 293 K): [ppm] $\delta = 22.3$ (Me), 30.1 (dd, $J = 10.3$ Hz, $J = 65.6$ Hz, CH_2), 45.5 (m, C^3), 74.4 (m, C^1), 109.4 (s, C^2), 125.6–140.1 (C_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121 MHz, 293 K): [ppm] $\delta = 23.0$ (d, $J = 36.5$ Hz, PPh_2), 67.6 (d, $J = 36.5$ Hz, $\text{P}(\text{O})\text{Ph}_2$). IR (Nujol): [cm^{-1}] $\nu = 1462$ s, 1439 s, 1377 s, 1131 m, 740 m, 692 m, 658 versus SIMS (NBA), cation: m/z ($I_{\text{rel.}}$ (%)) = 513 (100) [(mall)Ni(dppmO)] $^+$, 458 (20) [Ni(dppmO)] $^+$, 73 (49). SIMS (NBA), anion: m/z ($I_{\text{rel.}}$ (%)) = 235 (100) [SbF_6] $^-$.

4.3. Synthesis of halide- and water-free [BMIM][PF₆]

In a flask, 0.1 mol [BMIM]Cl is dissolved in 50 ml water. To this solution, 0.15 mol HPF₆ (65% solution in water) is added slowly at 0°C . The crude ionic liquid forms as a second liquid layer which is isolated by decantation. The ionic liquid layer is washed several times with portions of 50 ml water up to the point where the used washing water is neutral and contains no Cl^- anymore (check with AgNO_3 from acidic solution). To remove traces of water, the ionic liquid is dried under *vacuo* at 60°C overnight. The dryness of the resulting ionic liquid is confirmed by IR spectroscopy and Karl-Fischer titration.

4.4. Catalytic experiments

The amount of [(mall)Ni(dppmO)][SbF_6] is dissolved in the defined amount of solvent (CH_2Cl_2 or ionic liquid) at 25°C . The catalyst solution is transferred into the autoclave equipped with a magnetic stirring bar. The autoclave is pressurized with ethylene and heated to the reaction temperature. The oligomerisation reactions is carried out under constant ethylene pressure. After the reaction time the autoclave is cooled to -40°C and depressurized. The solvent and the low boiling products are collected by flash distillation and analyzed by GC using an internal standard. High boiling products remain in the autoclave. These are dried, weighted, and

hydrogenated (toluene, Pd on activated carbon, 40 bar H_2) for determination of maximum chain length and linearity.

4.5. Determination of ethylene solubility in ionic liquids

Ethylene solubility in the different solvents (CH_2Cl_2 and ionic liquids) were determined following a procedure that has previously been described by Mecking et al. [21] for the determination of ethylene solubility in various organic solvents. The autoclave (reactor 1) was charged with 10 ml of solvent under argon atmosphere and weighed. It was then pressurized with 50 bar of ethylene and stirred under constant pressure. After equilibration the autoclave was weighed again. To account for the mass of ethylene in the gas-phase, the solvent was replaced in another experiment with glass beads of equal volume, and the experiment was repeated. The difference in ethylene uptake yields the amount of ethylene dissolved in the solvent. This method implies as an approximation the assumption of constant volume of the liquid phase even under the applied ethylene pressure.

4.6. Determination of 1-olefin solubility in ionic liquids

The solubility of higher 1-olefins in the different ionic liquids was measured by $^1\text{H NMR}$ spectroscopy using the signal integration of the *N*- CH_3 group of the imidazolium cation and the signal integration of the olefinic protons of the olefin to determine the molar amount of olefin dissolved in the ionic liquid. From these data the mass% values given in Fig. 4 were calculated.

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