

The role of aluminum species in biphasic butene dimerization catalyzed by nickel complexes

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Abstract

The effect of the composition of the 1-butyl-3-methyl-imidazolium organochloroaluminate ionic liquid on the activity and distribution of the products of 1-butene dimerization catalyzed by a nickel complex under biphasic conditions is described. Three classes of ionic liquids have been employed, the first one with an aluminum (AlCl_3) molar fraction of 0.50, the second one with an aluminum molar fraction of 0.55 and the third one with an aluminum molar fraction of 0.65. These ionic liquids were modified with different amounts of AlEtCl_2 co-catalyst. An increase in the amount of co-catalyst added to the ionic liquid increases the global activity of the system, except for an AlCl_3 molar fraction of 0.50. Changing the cation from 1-butyl-3-methylimidazolium to 1-butyl-2,3-dimethylimidazolium gives rise to no modification in selectivity towards dimer products. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The use of “green” solvents that allow catalyst recovery and lower environmental impact and production costs is a great challenge in industrial processes. A strategic solution is the use of biphasic catalysis [1] using solvents that are immiscible with the reaction products, such as fluorinated compounds or ionic liquids. In the first case, a fluorinated-carbon phase contains dissolved reactants, catalyst, and the product phase has a limited solubility in the fluorinated phase. This system is somewhat expensive since it requires catalysts with specially modified ligands. In the second case, the catalyst is immobilized in an ionic liquid, IL, in which the products are immiscible [2], allowing quantitative recovery of the catalyst [3]. A successful example of an industrial application of ionic liquids is the DIFASOL process of IFP [4].

In the first oligomerization system reported using organochloroaluminate ionic liquids, Chauvin et al. [5] showed that the use of a “basic ionic liquid”, a term employed for ionic liquids with an aluminum molar fraction lower than 0.50, gives rise to no catalytic activity, due to the formation of an anionic species

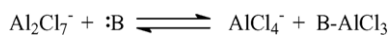
of the type NiCl_4^{2-} or NiCl_3L^- , whereas “acidic ionic liquids”, namely, those with an aluminum molar fraction higher than 0.50, display high activities. These authors also demonstrated [6] that the use of ionic liquids with an AlCl_3 molar fraction higher than 0.50, show an increase in activity with increasing aluminum molar fraction. Since then several works have been published employing acidic organochloroaluminate ionic liquids [7–11].

An undesirable feature of acidic ionic liquids is their reactivity towards basic ligands such as phosphines [6,11]. In order to minimize such a problem, Chauvin et al. [6] employed aromatic hydrocarbons as solvent exploiting the fact that it can be complexed by AlCl_3 , decreasing its intrinsic acidity, without changing the catalyst’s selectivity, as shown in Scheme 1.

Melton et al. [12], studying the electrochemical behavior of a buffered ionic liquid, observed that these systems have the same behavior of a neutral ionic liquid, with an AlCl_3 molar fraction of 0.50. Osteryoung et al., also studying the electrochemical behavior of buffered ionic liquids observed the decomposition of the AlCl_4^- species in the presence of bases, a phenomenon denominated as *latent acidity* [13,14].

Wasserscheid et al. investigated the catalyst $(\text{cod})\text{Ni}(\text{hfocat})$ (where cod is 1,5-cyclooctadiene and hfocat is 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) immobilized in a buffered ionic liquid [15], and it showed greater activity and selectivity than the unbuffered system.

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Scheme 1. Buffering effect of a base in a chloroaluminate ionic liquid.

Despite the existence of a host of information on the acidity of organochloroaluminate ionic liquids, there is a lack of a systematic approach on studying the effects of the addition of different amounts of co-catalyst on its bulk composition. Several studies on the acidity of organoaluminate ILs [6,15] did not take into account the interaction between the original anions and the added co-catalyst and, particularly, the effects on catalytic performance. Such a study defines the scope of the present work.

2. Experimental

All manipulations were performed under argon using standard Schlenk tube techniques. All solvents were purified and dried by standard procedures and distilled under argon.

2.1. Precatalyst preparation

The precatalyst $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ was prepared as previously described [16], by mixing 12 mmol of metallic nickel (Riedel) to 20 mmol of NOBF_4 (Acros), in acetonitrile as solvent. The solution was kept under stirring for 24 h, when unreacted nickel was removed with a magnetic bar and the acetonitrile was removed under reduced pressure. The complex was recrystallized from acetonitrile/ethyl acetate. After decantation, excess solvent was removed and the complex was dried under reduced pressure.

2.2. Ionic liquid preparation

2.2.1. Synthesis of 1-butyl-3-methylimidazolium chloride (BMIC) and 1-butyl-2,3-dimethylimidazolium chloride (BDMIC)

In this step, 0.10 mol of 1-methylimidazole or 1,2-dimethylimidazole (Acros), which had been previously distilled, were mixed with 0.12 mol of 1-chlorobutane (Acros), in 30 mL of acetonitrile. The solution was maintained under stirring and reflux for 48 h. After this period, unreacted 1-chlorobutane and acetonitrile were removed under reduced pressure. To the product 10 mL of acetonitrile were added, and the 1-butyl-3-methylimidazolium chloride (BMIC) or 1-butyl-2,3-dimethylimidazolium chloride (BDMIC) were precipitated by the addition of ethyl acetate. The solids were dried under reduced pressure.

2.2.2. Ionic liquid synthesis

For the synthesis of the ionic liquids (ILs) employed in this study, BMIC or BDMIC were slowly added over AlCl_3 , which had been sublimed once prior to use. The temperature was regulated so as not to exceed 30 °C. To complete the ionic liquid synthesis, the desired quantity of AlEtCl_2 , was added and the ionic liquid was kept under stirring overnight.

2.3. Catalytic runs

The catalytic runs were performed using a double-walled glass reactor equipped with magnetic stirring, a thermocouple, with continuous feed of 1-butene at 1.08 bar, 0.10 ± 0.01 mmol of precatalyst and 7 mL of cyclohexane at 10 °C. The temperature was controlled by a thermostatic circulation bath. After the system was purged with 1-butene, 3 mL of the ionic liquid were added, starting the dimerization reaction. The catalytic runs were performed in two cycles. In the first cycle stirring was stopped after 60 min, the phases were allowed to separate and the upper phase was withdrawal by cannula, then the reaction was reinitiated, for the second cycle, and maintained for a further 80 min.

The organic phase (withdrawal) was analyzed by gas chromatography. The selectivity determination as linear dimers (S_L), mono-branched dimers (S_{B1}) and di-branched dimers (S_{B2}), was performed on hydrogenated samples. The hydrogenation was made on a 1 mL sample of the organic phase to which was added 5 mL of methyl alcohol, Pd/carbon catalyst (Degussa), 40 atm of hydrogen and the reactor maintained at 60 °C for 16 h. Chromatographic analyses were performed on a Varian 3400 CX, equipped with a Petrocol DH capillary column: methyl silicone, 100 m long, i.d. 0.25 mm, and film thickness 0.5 μm. Analysis conditions: 50 °C for 30 min and heating rate of 5 °C/min until 250 °C, maintaining 5 min at 250 °C. The imprecision of the TOF values, defined as moles of converted butenes per mole of precatalyst and by reaction time (in h), was $\pm 10\%$, determined by at least two independent experiments in each case. The imprecision in dimerization selectivity reached $\pm 3\%$ and imprecision in dimers' composition was $\pm 1\%$.

3. Results and discussion

Varying the aluminum content in the melt can control the acidity of a chloroaluminate ionic liquid. This change in acidity is due to different aluminum species formed at different neat compositions. An ionic liquid is said to be *acidic* when species such as Al_2Cl_7^- and $\text{Al}_3\text{Cl}_{10}^-$ are present, and this would occur when the molar fraction of AlCl_3 is higher than 0.50. Following the same reaction pattern, adding AlEtCl_2 to an organoaluminate ionic liquid would generate analogous species such as $\text{Al}_2\text{EtCl}_6^-$ and $\text{Al}_3\text{EtCl}_9^-$ [17], depending on the amount of the alkylaluminum compound and this would also affect the acidity of the final IL.

The study of the influence of the acidity of the ionic liquid on 1-butene dimerization was made employing $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ as precatalyst. Initial experiments were made with neutral ILs, *i.e.*, ILs with a molar fraction of AlCl_3 of 0.50, with the addition of different amounts of AlEtCl_2 . These results are shown in Table 1.

As can be seen from Table 1, entries 1, 3 and 5, the selectivity towards dimerization and the selectivity within the dimer fraction is unaffected by an increase in the amount of AlEtCl_2 in the ionic liquid. This strongly suggests that at this AlCl_3 content (0.50), there is no change in the coordination sphere of the metal active site when the IL contains different amounts of AlEtCl_2 .

Table 1

Catalytic behavior of $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ dissolved in ionic liquids with a molar fraction of AlCl_3 of 0.50

Entry	Ionic liquid (molar fraction)	Cycle	TOF ^a (10^3 h^{-1})	$S_{\text{C}_8}^{\text{b}}$ (%)	S_{L}^{c} (%)	$S_{\text{B}_1}^{\text{d}}$ (%)	$S_{\text{B}_2}^{\text{e}}$ (%)
1	BMIC/ AlCl_3 / AlEtCl_2 (0.48/0.50/0.02)	1	5.1	95	8	58	34
2	BMIC/ AlCl_3 / AlEtCl_2 (0.48/0.50/0.02)	2	4.7	94	8	58	34
3	BMIC/ AlCl_3 / AlEtCl_2 (0.45/0.50/0.05)	1	5.7	95	7	59	34
4	BMIC/ AlCl_3 / AlEtCl_2 (0.45/0.50/0.05)	2	6.5	94	7	59	34
5	BMIC/ AlCl_3 / AlEtCl_2 (0.40/0.50/0.10)	1	6.1	95	8	58	34
6	BMIC/ AlCl_3 / AlEtCl_2 (0.40/0.50/0.10)	2	7.6	94	7	59	34

^a TOF = moles of converted butenes per mole of nickel and per hour.^b Selectivity in dimers.^c Selectivity in linear C8 products.^d Selectivity in mono-branched C8 products.^e Selectivity in di-branched C8 products.

co-catalyst. The recycle, *i.e.*, withdrawal of products and restart of the reaction, has no significant effect on the selectivities, as can be seen when comparing entries 1–2, 3–4, and 5–6. The selectivities remain the same, after two cycles showing that the catalytically active species maintain their structure throughout these reaction times.

The addition of different amounts of AlEtCl_2 to ILs with an AlCl_3 molar fraction of 0.50 has a small effect on the activity. It can be observed in Table 1 a slight increase in the TOF at higher AlEtCl_2 content, entries 1, 3 and 5, but it should be pointed out that the observed variation has a magnitude similar to the experimental error. Such observation leads us to the conclusion that the activity is related to the nature of the co-catalyst formed *in situ*, at this composition range, $\text{Al}_2\text{EtCl}_6^-$, and not to the amount of this compound.

This is not the case when considering recycling, *i.e.*, successive cycles of production and withdrawal and restarting of the oligomerization reaction. It can be seen; comparing entries 1 and 2, that the activity tends to decrease in the second cycle although entries 3–4 and 5–6 show an opposite trend. The interpretation of such behavior is that a minimal amount of co-catalyst is needed, and this is probably due to the alkylating capacity needed to maintain a significant amount of active species after recycle. For amounts of co-catalysts greater than 0.02 this minimal amount is present and, as a consequence, the amount of active species is still increasing during the different cycles of the reaction. Similar behavior has been described in the literature [11] and explanations such as a modification of the polarity of the media or a

modification of the aluminum counter anions in the ionic liquid forwarded as explanations.

When the molar fraction of AlCl_3 in the IL is increased from 0.50 to 0.55, the behavior of the system changes dramatically. The major change occurs in catalytic activity, which decreases markedly, when compared to systems with a lower content of AlCl_3 , as can be seen for the results of the behavior of a catalytic system for an IL with a molar fraction of AlCl_3 of 0.55 reported in Table 2.

Comparing the behavior of the ionic liquids with a molar fraction of AlCl_3 of 0.55, it could be observed that, as in case of ILs with an AlCl_3 molar fraction of 0.50, the selectivity towards dimerization (S_{C_8}) and within the dimers fraction does not change with the composition, except in the case of entry 8. The difference between the ILs with an AlCl_3 molar fraction of 0.50 and 0.55 is the presence of the species Al_2Cl_7^- besides the major anion AlCl_4^- . The Al_2Cl_7^- is considered to be noncoordinating [18,19], compared with AlCl_4^- and this is the probable reason for the absence of an effect on the selectivity. The absence of an effect of the composition on the selectivity in ILs in which Al_2Cl_7^- species are present is not a common feature in oligomerization reactions. Usually the presence of Al_2Cl_7^- results in some change in selectivity as a consequence of the abstraction of ligands from the catalyst by this species [6,11]. In the case of $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ it is probable that the actual catalyst has only aluminum species coordinated to the nickel core, even in ILs with an aluminum molar fraction of 0.50.

Table 2

Catalytic behavior of $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ dissolved in ionic liquids with a molar fraction of AlCl_3 0.55

Entry	Ionic liquid (molar fraction)	Cycle	TOF ^a (10^3 h^{-1})	$S_{\text{C}_8}^{\text{b}}$ (%)	S_{L}^{c} (%)	$S_{\text{B}_1}^{\text{d}}$ (%)	$S_{\text{B}_2}^{\text{e}}$ (%)
7	BMIC/ AlCl_3 / AlEtCl_2 (0.43/0.55/0.02)	1	1.5	94	10	58	32
8	BMIC/ AlCl_3 / AlEtCl_2 (0.43/0.55/0.02)	2	0.9	74	15	45	40
9	BMIC/ AlCl_3 / AlEtCl_2 (0.40/0.55/0.05)	1	2.8	96	9	58	33
10	BMIC/ AlCl_3 / AlEtCl_2 (0.40/0.55/0.05)	2	2.8	92	8	58	34
11	BMIC/ AlCl_3 / AlEtCl_2 (0.35/0.55/0.10)	1	4.7	92	8	56	36
12	BMIC/ AlCl_3 / AlEtCl_2 (0.35/0.55/0.10)	2	4.9	92	7	58	35

^a TOF = moles of converted butenes per mole of nickel and per hour.^b Selectivity in dimers.^c Selectivity in linear C8 products.^d Selectivity in mono-branched C8 products.^e Selectivity in di-branched C8 products.

Table 3
Catalytic behavior of $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ dissolved in ionic liquids with a molar fraction of AlCl_3 of 0.65

Entry	Ionic liquid (molar fraction)	Cycle	TOF ^a (10^3 h^{-1})	$S_{\text{C}_8}^{\text{b}}$ (%)	S_{L}^{c} (%)	$S_{\text{B}_1}^{\text{d}}$ (%)	$S_{\text{B}_2}^{\text{e}}$ (%)
13	BMIC/ AlCl_3 / AlEtCl_2 (0.30/0.65/0.05)	1	0.4	75	26	45	29
14	BMIC/ AlCl_3 / AlEtCl_2 (0.30/0.65/0.05)	2	0.3	64	20	43	37
15	BMIC/ AlCl_3 / AlEtCl_2 (0.25/0.65/0.10)	1	0.6	69	16	35	49
16	BMIC/ AlCl_3 / AlEtCl_2 (0.25/0.65/0.10)	2	0.7	76	14	44	42

^a TOF = moles of converted butenes per mole of nickel and per hour.

^b Selectivity in dimers.

^c Selectivity in linear C8 products.

^d Selectivity in mono-branched C8 products.

^e Selectivity in di-branched C8 products.

It is known that a fraction of the AlEtCl_2 present in the IL is extracted progressively into the organic phase [20], as a consequence of the equilibrium of the formation of charged chloroaluminate species. This is the probable explanation for the decrease in selectivity and activity in the case of entry 8. This system behaves much more like a Lewis acid, giving higher oligomers but with low activity.

Comparing the results of Table 2 with the analogues in Table 1 there is a meaningful loss in activity when the IL acidity increases. This also can be explained by the presence of Al_2Cl_7^- , which decreases the dimerization catalytic activity. Comparing entries 7, 9 and 11, it is clear the pronounced increase of the activity with the addition of AlEtCl_2 , showing a partial compensation of loss in activity by the presence of Al_2Cl_7^- with the increase of AlEtCl_2 content in the IL.

The systems using ILs with an AlCl_3 molar fraction of 0.65, shown in Table 3, have much lower activity than their analogues in Tables 1 and 2.

For the range of compositions described in Table 3 the main counteranions present in ionic liquids are Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$ and $\text{Al}_3\text{EtCl}_9^-$. As stated before, the decrease in dimerization selectivity can also be ascribed to the presence of these species, probably interacting with the metal, giving rise to the formation of higher contents of heavier products.

A plausible explanation for the decrease in butene dimerization activity with an increase of acidic species such as Al_2Cl_7^- should take into account that these species can

abstract hydrides from alkenes [21]. Such an observation was clear when, for example, hydrides were abstracted from alkenes promoting alkylating reactions [22]. It is well known that acidic ionic liquids can catalyze the oligomerization of light olefins [5,23], but to confirm such a possibility and to determine the profile of the products some experiments have been carried out as shown in entries 17 and 18, Table 4.

When an ionic liquid without co-catalyst is employed, entry 17, 18 g of yellow highly viscous heavy oligomers were formed, characteristic of a cationic oligomerization. The use of an ionic liquid with a molar fraction of 0.05 in AlEtCl_2 totally suppressed the formation of such oligomers, as can be seen in entry 18. This behavior is explained when one considers, as the first stage, a hydride abstraction on the olefin by Al_2Cl_7^- , generating an allylic cation, with a subsequent alkylation in a second stage consuming the co-catalyst and decreasing the possibility of precatalyst activation and, consequently, decreasing the activity. This is in agreement with the dependence of activity on the amount of AlEtCl_2 in acidic ionic liquids, as is shown in Scheme 2.

This scheme can explain that increasing the AlCl_3 content in ILs decreases the activity due to the lower availability of co-catalyst, needed to alkylate the transition metal in order to promote the oligomerization reaction [8]. The proposed scheme also explains the activity dependence on co-catalyst content on acidic ionic liquids.

Table 4
Catalytic behavior of $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ dissolved in different chloroaluminate ionic liquids and control runs without transition metal catalyst

Entry	Ionic liquid (molar fraction)	Time (min)	TOF ^a (10^3 h^{-1})	$S_{\text{C}_8}^{\text{b}}$ (%)	S_{L}^{c} (%)	$S_{\text{B}_1}^{\text{d}}$ (%)	$S_{\text{B}_2}^{\text{e}}$ (%)
17	BMIC/ AlCl_3 (0.35/0.65) ^f	45	– ^{g,h}	–	–	–	–
18	BMIC/ AlCl_3 / AlEtCl_2 (0.30/0.65/0.05) ^f	60	0 ⁱ	–	–	–	–
19	BMIC/ AlCl_3 / AlEtCl_2 / NaCl (0.41/0.41/0.09/0.09)	60	– ⁱ	–	–	–	–
20	BMIC/ AlCl_3 / AlEtCl_2 /2,6-lutidine (0.41/0.41/0.09/0.09)	60	– ⁱ	–	–	–	–
21	BDMIC/ AlCl_3 / AlEtCl_2 (0.45/0.50/0.05)	60	3.3	95	7	59	34

^a TOF = moles of converted butenes per mole of nickel and per hour.

^b Selectivity in dimers.

^c Selectivity in linear C8 products.

^d Selectivity in mono-branched C8 products.

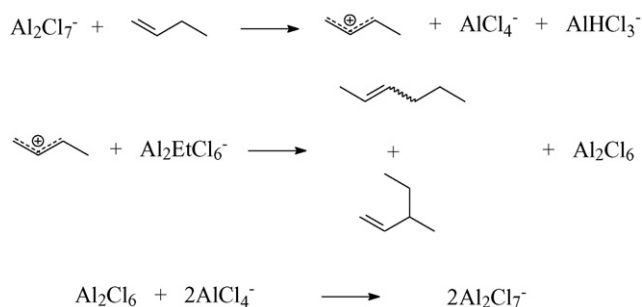
^e Selectivity in di-branched C8 products.

^f Without catalyst.

^g 18 g of highly viscous yellow liquid obtained as product.

^h TOF is not calculated once the oligomerization is of cationic nature.

ⁱ No products are obtained after 60 min.

Scheme 2. Influence of Al_2Cl_7^- on butene dimerization.

It is noteworthy that some authors [15] proposed the use of buffered ionic liquids as a way of improving activity in oligomerization reactions, suppressing cationic side oligomerizations. Not only an improvement in activity, but also in selectivity, in 1-butene dimerization, was achieved in such systems. Such buffered systems have no co-catalyst in their composition. In order to evaluate if buffered neutral-based ionic liquids containing AlEtCl_2 would grant an additional improvement in activity or even in selectivity, two buffering agents were tested, as in entries 19 and 20. Both buffering agents demonstrated inhibiting action, suppressing the catalytic activity. This shows that neutral ionic liquids modified by co-catalyst addition in their composition are the best choice for dicationic nickel precatalyst in oligomerization reactions.

A common problem faced in catalytic reactions carried out in ionic liquids based on 1,3-dialkylimidazolium salts is the formation of carbenes [24,25] through deprotonation on position 2 of the imidazolium ring. Some authors [26] explored such possibilities by preparing precatalysts based on heterocyclic imidazolium based carbenes, but these complexes exhibit no activity in homogeneous media. When these precatalysts were immobilized in an ionic liquid, they exhibited high activity in propene and butene dimerization. This different behavior in homogeneous and biphasic media was attributed to the formation of imidazolium based carbenes, through oxidative addition on nickel, regenerating the catalyst. The values of activity and selectivity in butene dimerization are quite similar to those described in this work, $S_L = 11.5\%$, $S_{B1} = 31.7\%$ and $S_{B2} = 56.8\%$. Such similarity can suggest that similar catalytically active species were formed in both cases. Alternatively, it should be taken into account that aluminum species can also coordinate to a metal, acting as ligands in catalytically active species [27,28]. In order to verify if the observed selectivity is due to the formation of a carbene or to the coordination of aluminum species to nickel, an ionic liquid with the 2 position of the imidazolium ring blocked by a methyl group was prepared, in order to avoid carbene formation at this position. The result of its catalytic run is shown as entry 21, Table 4. Comparing the result of entry 21, Table 4, with entry 3, Table 1, there is no difference in selectivity, indicating that the structure of the catalytically active species is the same in both cases. This is indicative that, despite the possibility of carbene formation in ionic liquids, they are probably not coordinated to the catalytically active species, and the selectivity

towards dimers of 1-butene is determined by the coordination of aluminum species to the nickel center.

4. Conclusion

It has been observed that neutral based ionic liquids, AlCl_3 with a molar fraction of 0.50 are the best immobilization media for dimerization reactions, but for catalyst recycling there is a minimal AlEtCl_2 content in order to avoid a drop in catalyst activity and selectivity after the recycle of the catalytic system. The possibility of the intervention of carbene species in the IL has been ruled out based on the selectivity results and on specific tests with C2-blocked imidazolium ionic liquids. ILs are shown to be outstanding reaction media for catalytic oligomerizations using $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ as precatalyst. The nature of the interaction of the co-catalyst with a chloroaluminate ionic liquid fulfills an important role in achieving the best performance in oligomerization reactions.

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