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# The Use of Ionic Liquids in the Oligomerization of Alkenes

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/57478>

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## 1. Introduction

The more and more stringent quality standards of motor fuels, targeting the reduction of harmful material emission of the vehicles, require the development of new technologies for fuel production or improvement of the existing ones. The need for environmentally friendly, relatively clean-burning and practically heteroatom-free, high *n*- and *i*-paraffin containing blending fractions has been increasing.

From the options to convert light hydrocarbons ( $C_3$ – $C_6$  paraffins and olefins) of lower value to high quality blending components, oligomerization is one of the most promising methodologies. It provides extra flexibility to respond to changes in market demands with regards to the required gasoline:diesel ratio.  $C_3$ – $C_5$  olefins obtained by fluid catalytic cracking can be oligomerized to produce branched products which have higher octane numbers. The need for an increased overall diesel fuel yield can be addressed by  $C_3$ – $C_5$  olefin oligomerization operated in the trimer or tetramer mode, followed by hydrogenation of the products.

Beside the application as blending components in diesel fuels, triisobutenes are considered to be highly useful for the synthesis of specialty chemicals including dodecylbenzene, base oils and solidifying agents for epoxy resins. Oligomerization, and further hydrogenation of other olefins, such as 1-octene and 1-decene results in the formation of high viscosity index (good lubricating properties) synthetic base oils with low pour point and good oxidative stability.

The main challenges in the design of catalysts for oligomerization are focused to reach high conversion and high selectivity. Consequently, several catalysts have been developed for the

oligomerization of lower alkenes. [1] Both Brønsted and Lewis acids have been used in either homogeneous or heterogeneous phase. Transition-metal complexes, such as Ni-based homogeneous catalysts containing phosphine ligands have also been developed. Ionic liquids were introduced first, as highly polar media, to ensure catalyst recovery due to biphasic conditions.

In recent years the use of room-temperature molten salts, or ionic liquids, has received increasing attention. The ionic liquids are good solvents for inorganic complexes (catalysts) while being immiscible with most hydrocarbons. As such, they provide a nonaqueous alternative for two-phase catalysis. Ionic liquid solvents eliminate the need to use volatile organic solvents. Furthermore, the nearly infinite combinations of suitable cations and anions lead to the possibility of tailoring their properties.

However, ionic liquids may serve not only as solvents, but also as catalysts during the oligomerization reaction. Both Lewis and Brønsted acidic ionic liquids have been used efficiently. Another possibility is the development of supported ionic liquid phases to combine the advantages of the ionic liquid with heterogeneous catalysis.

In the present chapter, after a short review of the importance and mechanism of light olefin oligomerization, the use of ionic liquids as solvents and catalysts in oligomerization reactions is presented. The effect of the composition of ionic liquids on the catalytic activity and selectivity is discussed in detail.

## 2. Industrial relevance of oligomerization of lower alkenes

Oligomerization of light olefins is an important alternative for the production of higher molecular weight hydrocarbon mixtures useful as fuels (e.g. gasoline or diesel). [2] It makes possible the upgrading of low value components of plant process streams, e.g. from fluid catalytic cracking, from cracking of polymers or wastes or from Fischer-Tropsch C<sub>3</sub>-C<sub>6</sub> olefins.

During oligomerization of light olefins, different boiling point range isoolefins can be produced. Gasoline, jet fuel, diesel gas oil and base oil boiling point range components can be formed depending on the level of oligomerization. They can be transformed to isoparaffins by hydrogenation. Because of the constant growth of the energy demand of transportation, there is an increasing need for the production of isoparaffins.

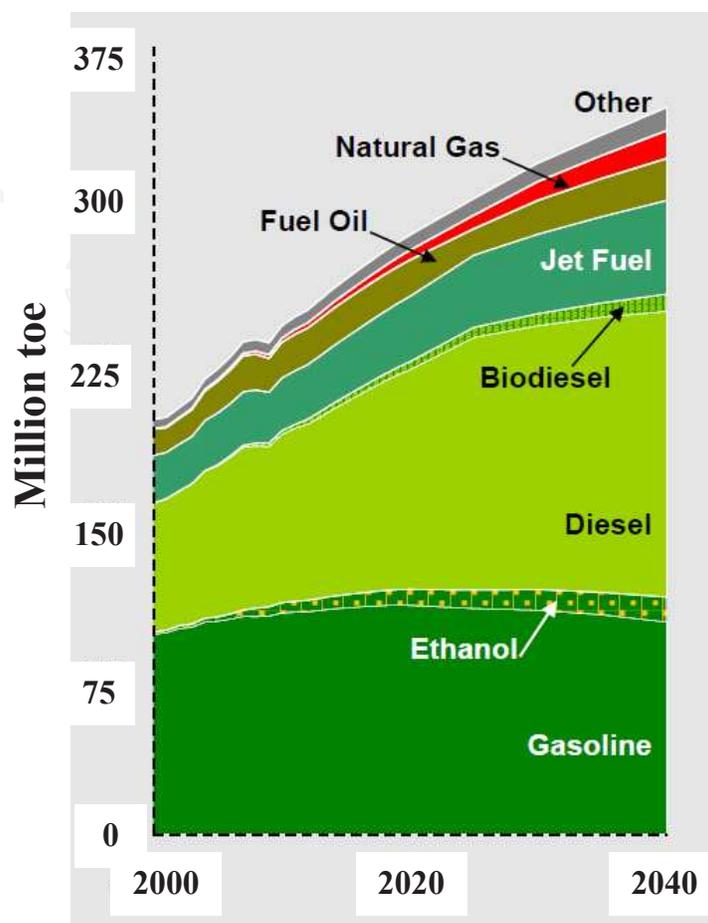
Inland, aerial and waterway mobility is a keystone of sustainable development. To operate the equipment of mobility, internal combustion engines will be used (dominant share ≥85%) based on forecasts until 2030-2035. [3]

Intermittent-duty engines are used in inland and waterway transport, while aircrafts are operated by continuous jet engines. From the former, the Otto- and Diesel-engines are the most prevalent. The operational materials of these engines are the motor fuels and, in a wider sense, lubricants and other materials (e.g. oxygen source, refrigerants), too. [4]

The quantity of the fuel used is in accordance with the type of the drive. [5,6]

Based on the fuel demand (Figure 1), liquid hydrocarbons (engine gasoline, diesel gas oil) are used in the widest range in inland transport. They must satisfy the most important general and special (see also Table 1 and Table 2) requirements, such as:

- long-time availability of quality and quantity all over the world
- good combustion properties
  - high octane number (gasoline)
  - high cetane number (Diesel fuels)
  - relatively low combustion temperature (lower amount of NO<sub>x</sub> formation; lower load of construction materials)
  - lower total harmful material emission, *etc.*
- very low sulphur content ( $\leq 10$  mg/kg)
- reduced aromatic content
  - gasoline: benzene content  $\leq 1.0$  v/v%; total aromatic content  $\leq 35$  v/v%
  - Diesel fuels: polyaromatic content  $\leq 8$  %
- reduced olefin content
- gasoline  $\leq 18$  v/v%
- good blending ability with alternative components (not only with hydrocarbons but also with e.g. oxygen containing compounds)
- good additive sensibility and compatibility with additives (e.g. nozzle, valve and combustion chamber clearness)
- compatibility with motor oils
- fewer harmful matters in the exhaust gas
- user-friendly
- secure utilisation
- easy biodegradation
- environmentally friendly (non toxic)
- low book-cost, *etc.*



**Figure 1.** Changing demand of fuel by type (toe: tonne of oil equivalent)

Based on these requirements, it can be unequivocally stated that it is only the quantity of paraffins (mainly iso- and cycloparaffins and, with less importance, *n*-paraffins) that is not limited directly or indirectly in fuels. The concentration of cycloparaffins with suitable boiling points is low in crude oil and their synthesis is still expensive. [4] As a consequence, the most important components of gasoline and diesel gas oils are mixtures of different carbon number (different boiling point) isoparaffins or high isoparaffin content fractions, from the aspect of performance properties, environment protection and health. For example, gasoline boiling point range isoparaffins have high octane number and energy content (Figure 2), [4,7] their sensibility is low, they are practically sulphur and aromatic free, less toxic and because of their 'cleaner ignition', lead to the formation of less harmful material. Isoparaffins in diesel gas oil boiling point range have high energy content and cetane number (Figure 3) and they have good flow properties even at low temperature (low freezing point) (Figure 4). [8,9] Moreover, they are the most suitable hydrocarbons from the aspect of environmental protection. These properties are due to their high hydrogen content ( $C_nH_{2n+2}$ ) and consequently low carbon content, their relatively easier biodegradation and low toxicity.

property	European Union				United States			WWFC
	EN 228 (1993)	EN 228 (2000)	EN 228 (2005)	EN 228 (2013)	RFG Phase II. 2012	CARB Phase 3 (2004/ 2006)	CARB Phase 3 (2009)	5. category (2012)
maximum sulphur content, mg/kg	500	150	50/10	10	80/30	60/30	30/20/15	10
maximum aromatic content, v/v%	-	42	35	35	-	35	35	35
maximum olefin content, v/v%	-	18	18	18	-	10	10	10
maximum benzene content, v/v%	5.0	1.0	1.0	1.0	0.62/1.3 <sup>a</sup>	1.1	0.7	1.0
maximum oxygen content, %	-	2.7	2.7	2.7/3.7	2.7/3.5	1.8-3.5 <sup>b</sup>	1.8-3.5 <sup>b</sup>	2.7
maximum ethanol content v/v%	-	5.0	5.0	5.0/10.0	10.0	-	-	5.0/10.0
maximum Reid vapour pressure, kPa	35-100	60/70	60/70	45-105	44-69	44-50	41-50	45-105

CARB: California Air Resources Board, WWFC: World Wide Fuel a: Commitment of crude oil refinery, b: Prohibited since 01. 01. 2004.

**Table 1.** Quality requirement changes of gasoline

Property	European Union				United States		WWFC
	EN 590 (1999)	EN 590 (2000)	EN 590 (2005)	EN 590 (2009)	Federal ASTM D 975-13 No. 2-D; S-15	CARB (2008)	5. category (2012)
minimum cetane number	48	51	51	51	40	53	55
maximum density at 15°C, kg/m <sup>3</sup>	820-860	820-845	820-845	820-845		-	820-840
maximum sulphur content, mg/kg	500	350	50.0/10.0	10.0	15	15	10.0
maximum total aromatic content, %	-	-	-	-	35.0 (m/m%)	10	15
maximum polyaromatic content, %	-	11	11	8	-	3.5	2.0
maximum distillation recovery (95%) temperature, °C	370	360	360	360	338 (90 v/v%)	-	350
maximum biodiesel (FAME-) content, v/v%,			5.0	7.0	5.0		not allowed

CARB: California Air Resources Board, WWFC: World Wide Fuel Charter

**Table 2.** Quality requirement changes of diesel gas oils

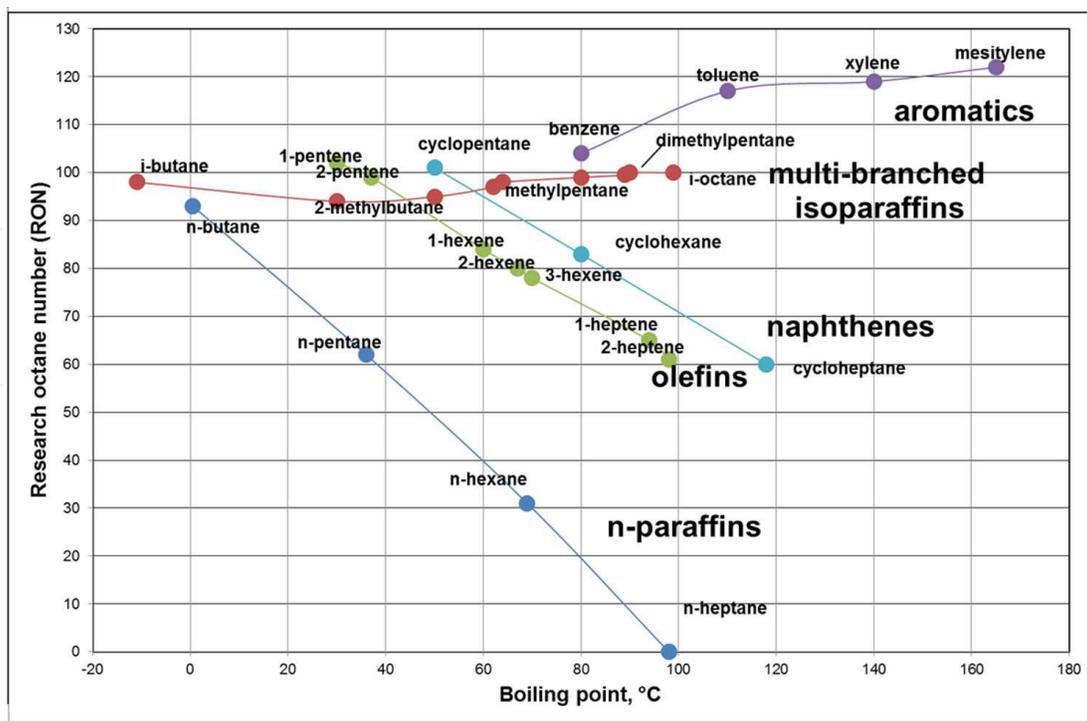


Figure 2. Research octane numbers of different hydrocarbons

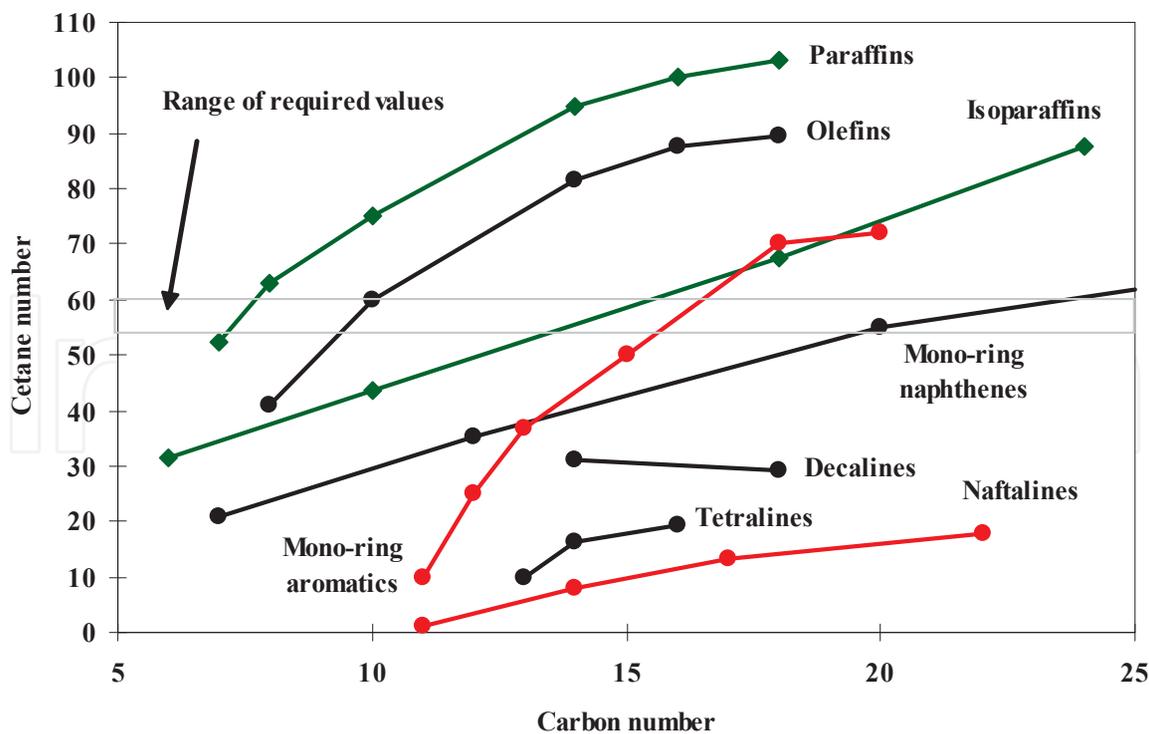
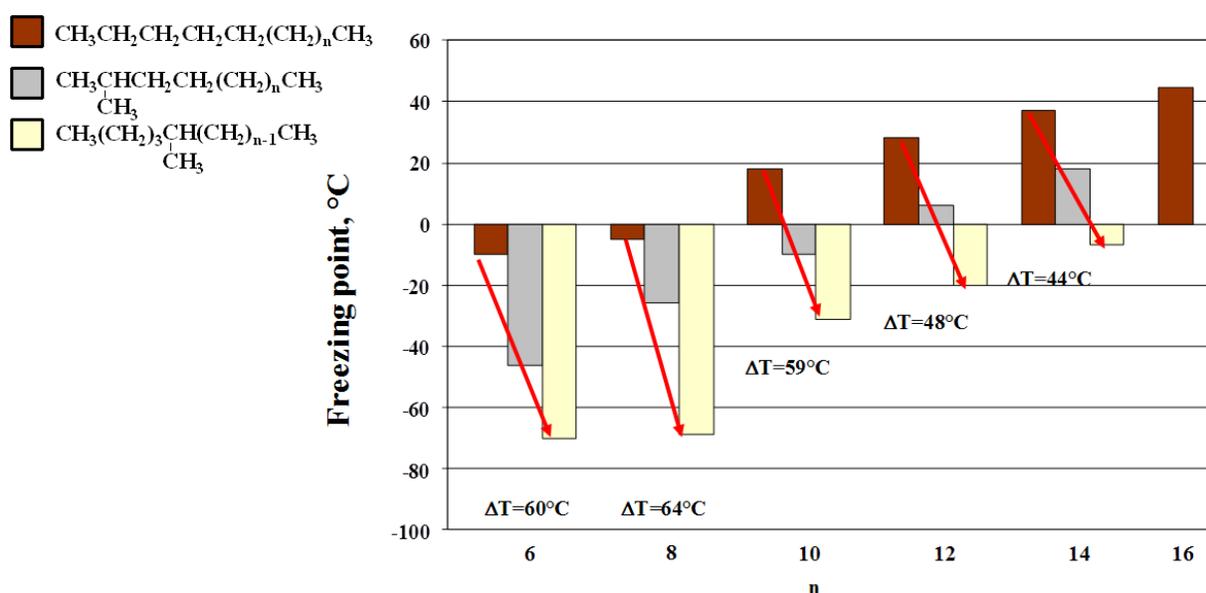


Figure 3. Cetane numbers of different hydrocarbons



**Figure 4.** Freezing points of different hydrocarbons

Isoparaffin hydrocarbons are of key importance not only as energy carriers but also as suitable lubricants in case of engine oils. From the main components of engine oils (base oil and additives), hydrocarbon based lubricating oils have 65-80% share. From the aspect of performance properties, paraffin hydrocarbons and especially isoparaffins with a proper boiling point range are the most suitable constituents (Table 3.). [10, 11] These hydrocarbons have excellent lubricant properties (high viscosity index), good or suitable flow properties (-65°C – -20°C), low evaporation loss, moreover, they are aromatic and sulphur free [12].

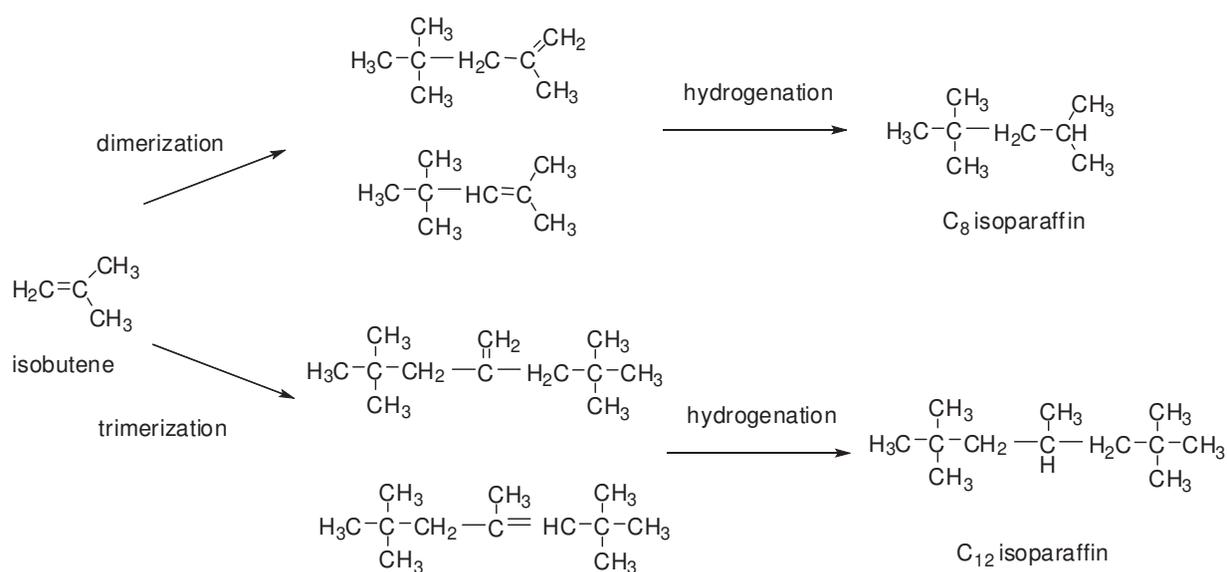
property	base oil					
	conventional	HC-1	HC-2	HC-3	HC-4	PAO
kinematic viscosity, (100°C) mm <sup>2</sup> /s	4	4	4	4	4	4
viscosity index	100	105	125	130	140	125
volatility (NOACK), %	23	18	14	13	11	12
flowpoint, °C	-15	-15	-18	-20	-30	-65
n- and i-paraffins, %	25	30	55	75	100	96
aromatics, %	24	05	0.3	0.1	0	-
sulphur content, %	<0.3	<0.1	<0.1	<100	<10	<1

HC-1:hydrocracking base oil; HC-2: rigorous hydrocracking base oil; HC-3: hydroisomerized paraffinic base oil, HC-4: Fischer-Tropsch paraffinic base oil, PAO: poly(alpha-olefins)

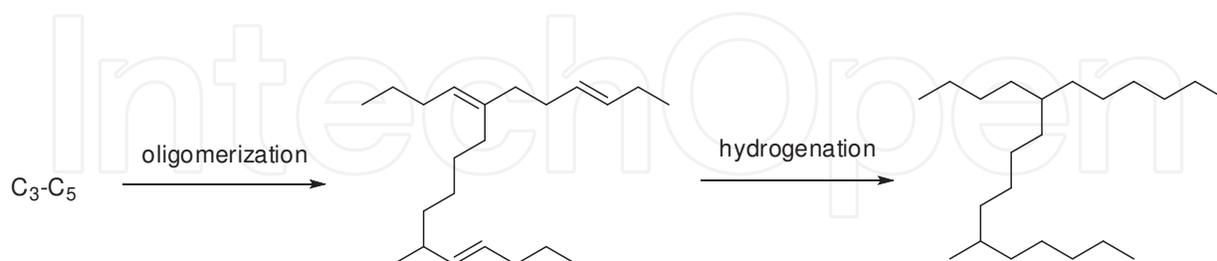
**Table 3.** Properties of different base oils

There are a lot of possibilities to produce isoparaffin rich fractions with different boiling point range:

- alkylation of isobutene with olefins (naphtha blending components)
- isomerisation of *n*-paraffins with suitable carbon number (C<sub>5</sub>-C<sub>7</sub> naphtha fractions, gas oil fraction)
- hydrocracking of higher molecular weight hydrocarbon mixtures
- suitable level oligomerization of light olefins followed by hydrogenation to isoparaffins (indirect alkylation in case of naphthas, gas oil targeted oligomerization and hydrogenation; base oil targeted oligomerization and hydrogenation) (Scheme 1, Scheme 2).

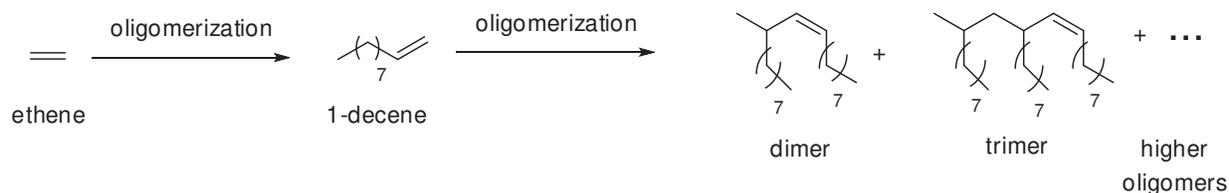


**Scheme 1.** Synthesis of naphtha boiling point range (C<sub>8</sub>) and jet fuel/gas oil boiling point range (C<sub>12</sub>) isoparaffins by an oligomerization – hydrogenation reaction sequence, starting from isobutene



**Scheme 2.** Base oil targeted oligomerization and hydrogenation of light olefins

Poly- $\alpha$ -olefins (PAOs), used as lubricant base oils, are synthesized by a two-step reaction sequence from linear  $\alpha$ -olefins derived from ethene (Scheme 3.). PAOs have good flow properties at low temperatures, relatively high thermal and oxidative stability, low evaporation losses at high temperatures, higher viscosity index, good friction behavior, good hydrolytic stability and good erosion resistance.



**Scheme 3.** Synthesis of poly- $\alpha$ -olefins (PAOs)

In summary, oligomerization of olefin hydrocarbons has an important role in the production of operational materials of internal combustion engines, and its importance is growing further. A great advantage of this method is that the quantity of each product can be controlled with the level of oligomerization. It makes the flexible adaptation to the market demands possible.

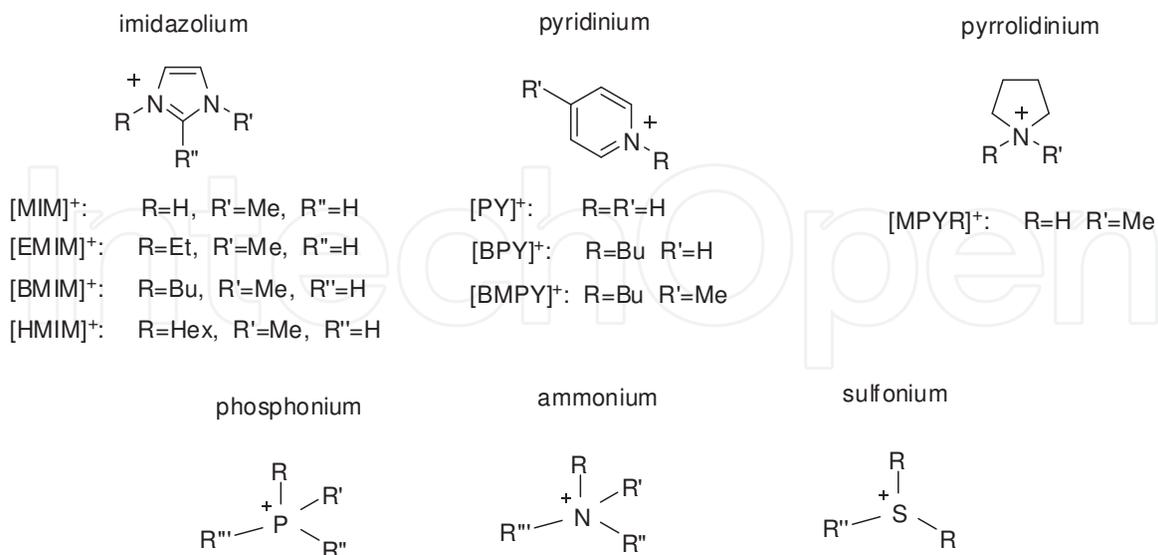
Beside the production of valuable blending components for fuels in petroleum refineries, oligomerization can be used for the large scale synthesis of fine chemicals and intermediates in the petrochemical industry. Linear  $C_8$ -olefin dimers are highly-desirable intermediates for the production of  $C_9$ -plasticizers, exhibiting better thermal properties than branched isomers. Oligomerization of ethene producing higher  $\alpha$ -olefins also represents an important industrial process, as the products, depending on the chain length, can be used as intermediates for plastics, plasticizers, surfactants.

During the quest for sustainable technologies for the production of oligomers, research concerning the use of ionic liquids as solvents and/or catalysts came into focus.

### 3. Main features of ionic liquids used in oligomerization reactions

Ionic liquids (ILs) are salts consisting of bulky organic cations and inorganic or organic anions. (Figure 5 shows the general formulas of the most commonly used ILs, as well as the structures of the compounds mentioned in this chapter.) They melt at relatively low temperature, usually below 100 °C. They are good solvents for polar organic molecules and inorganic salts but they do not dissolve apolar compounds. These properties, together with their ability to stabilize transition metal complexes in low oxidation states, make them ideal solvents for transition metal catalyzed reactions. [13] When the polarity of the products are sufficiently low, biphasic reactions take place. After the completion of the reaction, the products can be separated by simple decantation and the metal catalyst remains in the IL phase that can be reused. ILs have negligible vapor pressure and they are not flammable which makes them very easy and safe to handle. Mainly because of their low volatility, they are considered to be 'green solvents'. However, their toxicity, investigated more thoroughly only recently, [14] should also be taken into account. Because of the great variety of anion – cation pairs, and the diversity in the side chains of the cations, an almost infinite IL combinations can be produced. Task-specific ILs are developed by the fine-tune of their physical and chemical properties through a careful choice of the structure of the cation-anion pair.

## Cations



## Anions

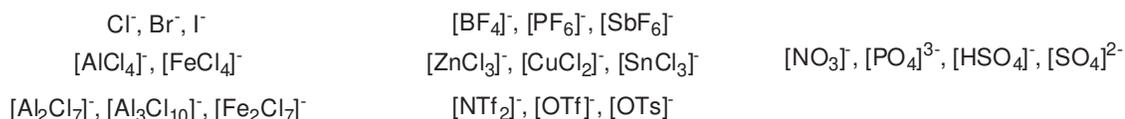


Figure 5. Common cations and anions of ILs

From the point of view of oligomerization of alkenes, mainly acidic ILs (Figure 6) are of interest. [15] Acidity may be due either to the anion or to the cation of the IL. [16]

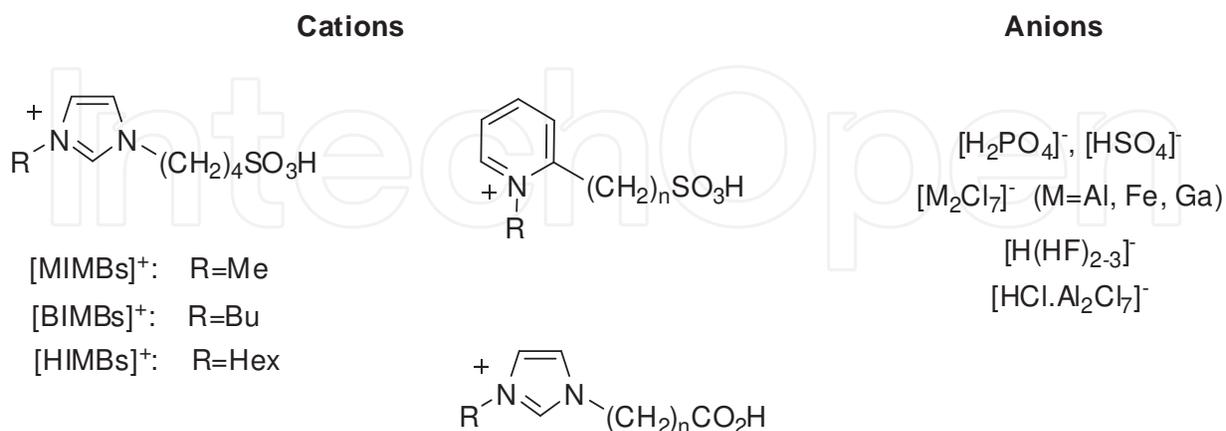


Figure 6. Cations and anions of acidic ILs

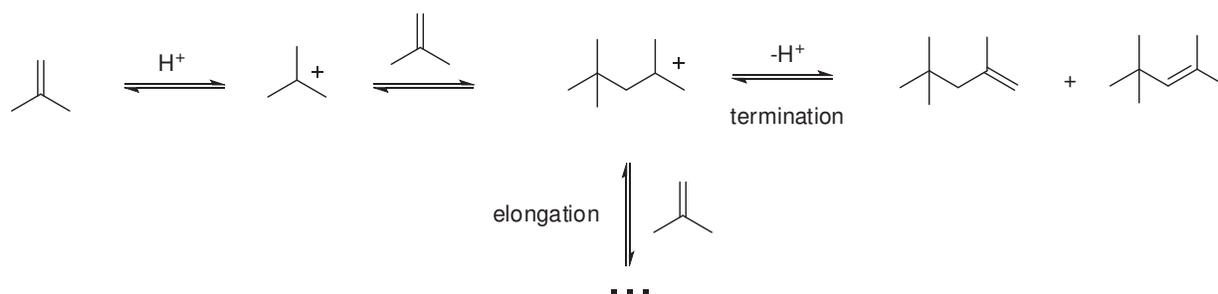
ILs with polynuclear metallic anions, such as chloroaluminate, chloroferrate or chlorozincate ions, show Lewis acidity [16] and, in the presence of protons, superacidity. [17] Brønsted

acidity can be achieved by the addition of Brønsted acids such as HF or HCl into halide based ILs. The advantage of these systems lies in the fact that by supporting the acid in the ILs, its volatility can be reduced.

Acidity of the ILs depends greatly on the structure of the cations, too. [MIM][BF<sub>4</sub>] shows higher acidity compared to dialkylimidazolium ILs. [18] At the same time, Brønsted acidic ILs are usually prepared by the introduction of alkane sulfonic acid or carboxylate acid groups as side chains of the cations (Figure 6).

#### 4. Oligomerization mechanisms relevant in IL solvents

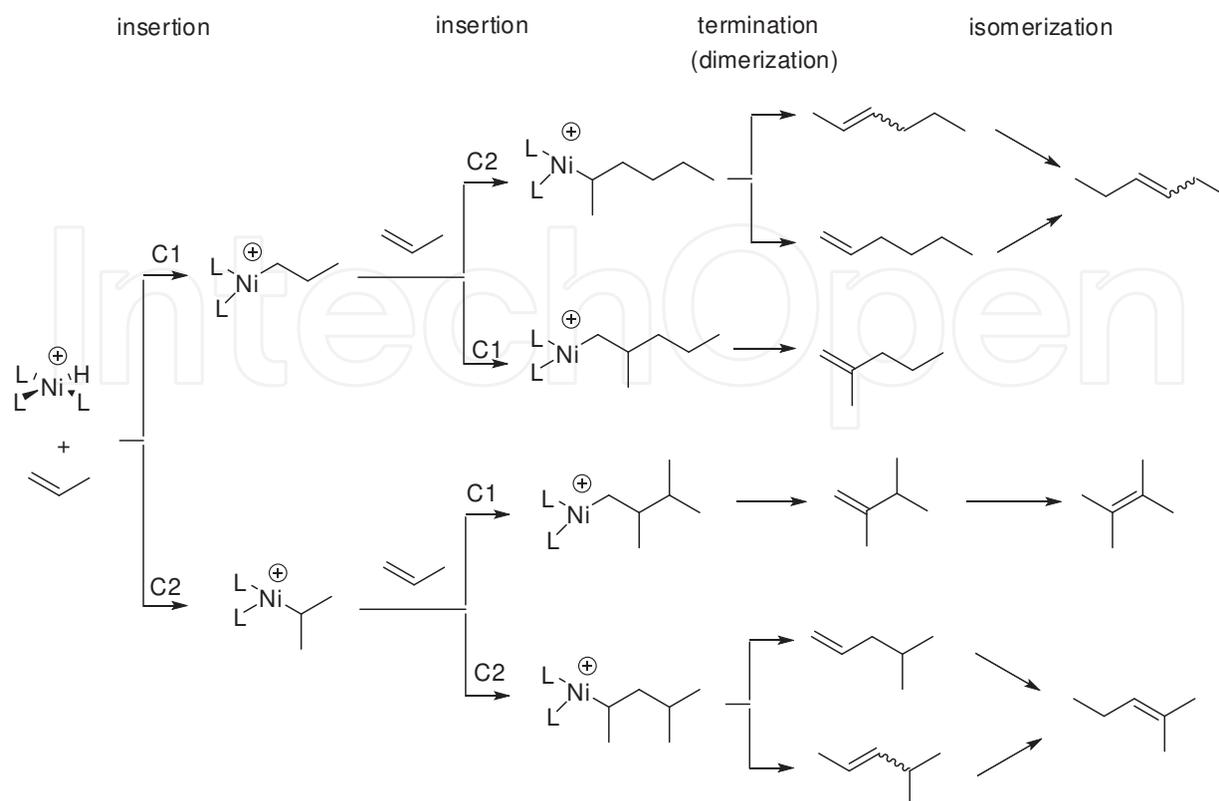
In oligomerization of alkenes, the most widely used methods involve cationic oligomerization in the presence of acids and transition metal catalyzed oligomerization. [19] In the first case, a carbocation intermediate is formed by the transfer of a proton from the acid catalyst to the alkene (for oligomerization of isobutene, see Scheme 4). Then the carbocation acts as an electrophile and reacts with the alkene to form another carbocation produced from two monomers. Termination happens when the dimeric carbocation loses a proton. When the carbocation is reasonably stable, this termination reaction is slower than chain elongation and the reaction leads to a trimer then a tetramer and finally a polymer.



**Scheme 4.** Mechanism of cationic oligomerization of isobutene

In the transition metal catalyzed reaction the catalytically active species is regenerated after coordination of the olefin, chain growth and termination by  $\beta$ -elimination, producing the primary oligomerization product. Dimerization of alkenes can be described as two successive insertions of the olefin in the catalytic species. [20]

In the industrial Dimersol<sup>TM</sup> process, the active catalyst is formed in situ by the reaction of a nickel (II) salt with an ethylaluminumhalide derivative. In the first step, insertion of either the C1 or C2 carbon of the alkene can occur, leading to various linear or branched dimers (for the mechanism of propene dimerization, see Scheme 5). At the same time, the nickel-complexes are active catalysts in isomerization, leading to further isomeric products. [19] The regioselectivity of dimerization can be directed by the addition of appropriate ligands. For example, in nickel-catalyzed oligomerizations sterically demanding phosphines favor the formation of highly branched oligomers.



**Scheme 5.** Mechanism of nickel-catalyzed dimerization of propene

The main challenges in the design of catalysts for oligomerization are focused to reach high conversion and high selectivity. Although transition metal catalysts can efficiently be fine-tuned to achieve these goals, a great drawback of the homogeneous systems lies in the problem of catalyst recovery and recycle. The use of a two-phase solvent mixture is an attractive alternative, as it enables catalyst separation and reuse. ILs were introduced first in oligomerization reactions as co-catalysts, as well as polar solvents ensuring biphasic nickel-catalyzed reactions. [21]

## 5. The use of ILs as solvents in oligomerization catalyzed by organometallic complexes

### 5.1. Oligomerization with Ni catalysts

Chloroaluminate ILs, composed of imidazolium [22-34] or pyridinium [33, 35] halides,  $AlCl_3$  and, in most cases, an alkylaluminum compound ( $AlEtCl_2$  or  $AlEt_2Cl$ ), act both as a medium for catalyst immobilization and nickel activator (Table 4). The cationic nickel active species is immobilized in the ionic phase without the need of a special ligand. Because of the high solubility of the Ni-complex but poor solubility of the products in the IL, complete separation of the catalyst can be achieved by simple decantation. In principle, the recovered catalyst/IL phase can continuously be reused maintaining its catalytic activity and selectivity.

Activities of catalysts in organic solvents were found to be considerably lower than those obtained from the same nickel precursors immobilized in an IL. [22]. This can be explained by an increase in the electrophilic nature of the nickel metal center by the weak coordinating ability of chloroaluminate anions.

The efficiency of the IL/catalyst system depends noticeably on the composition of the chloroaluminate IL. In ILs with an aluminum molar fraction lower than 0.50 ('basic ionic liquids'), the presence of an excess of coordinating chloride anions inhibits catalytic activity due to the formation of stable anionic species such as  $\text{NiCl}_4^{2-}$  and  $\text{NiCl}_3\text{L}^-$ . [23, 24]



Acidic chloroaluminates, with an aluminum molar fraction higher than 0.50, show enhanced activity. At the same time, in acidic ILs composed of  $[\text{BMIM}]\text{Cl} / \text{AlCl}_3$ , the formation of multinuclear species, such as  $[\text{Al}_2\text{Cl}_7]^-$  or  $[\text{Al}_3\text{Cl}_{10}]^-$  were detected. In the presence of  $[\text{Al}_2\text{Cl}_7]^-$ , an abstraction of the phosphine ligand, ensuring high branching in the product mixture, from the coordination sphere of the metal occurs [24] that alters the selectivity of the reaction.



To avoid this, a weak competitive base, an aromatic hydrocarbon [24, 25] that did not interfere with the cationic nickel active species, was added to the reaction mixture. Thus, the acidity and the distribution of aluminum anionic species could be controlled due to the coordination of  $\text{AlCl}_3$  to the aromatic ring.



As another disadvantage, the presence of  $[\text{Al}_2\text{Cl}_7]^-$  leads to the formation of yellow highly viscous heavy oligomers, characteristic of a cationic oligomerization, even in the absence of a Ni-precursor, [23, 26] arising from the superacidity of proton contamination of the ionic liquid.

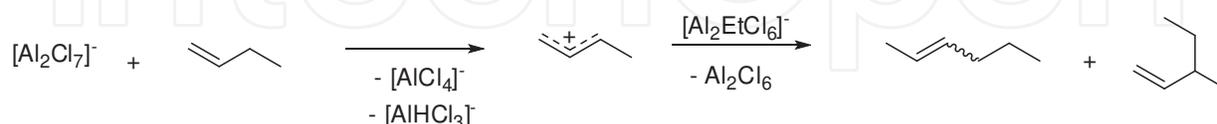


First, these problems were eliminated by the use of  $\text{AlEtCl}_2$  instead of  $\text{AlCl}_3$ . In these ILs, both the formation of higher oligomers, and the loss of phosphine ligands could be avoided. The latter statement was based on the fact, that selectivity of the reaction was shifted towards 2,3-dimethylbutenes during dimerization of propene, characteristic in the presence of catalysts with bulky ligands. [23]

In  $[\text{BMIM}]\text{Cl} / \text{AlEtCl}_2 / \text{AlCl}_3$  systems, ethylaluminum species such as  $[\text{AlEtCl}_3]^-$ ,  $[\text{Al}_2\text{Et}_2\text{Cl}_5]^-$ ,  $[\text{Al}_2\text{EtCl}_6]^-$  and  $[\text{Al}_3\text{Et}_3\text{Cl}_7]^-$  [36] are formed, depending on the amount of the alkylaluminum

compound. The composition of the mixture greatly affects the acidity of the final IL, so an adjustment of the AlEtCl<sub>2</sub> to AlCl<sub>3</sub> ratio is necessary in order to optimize the efficiency of the catalyst/ionic liquid system.[24, 26]

Cationic side reactions in [BMIM]Cl / AlCl<sub>3</sub> ILs could totally be suppressed by the addition of AlEtCl<sub>2</sub>, even in a molar fraction as low as 0.05. [26] This behavior was explained by a hydride abstraction on the olefin by [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup>, generating an allylic cation (Scheme 6), with a subsequent alkylation consuming the co-catalyst.



**Scheme 6.** The role of alkylaluminum derivatives in the suppression of cationic oligomerization

However, the loss of AlEtCl<sub>2</sub> may decrease the possibility of precatalyst activation in nickel-containing systems and consequently decreases their activity. This explanation is in agreement with the observation that increasing the AlCl<sub>3</sub> content of the ILs decreases the activity, due to the lower availability of the co-catalyst, necessary for the alkylation of the nickel precursor.

Generally, the use of slightly acidic [BMIM]Cl / AlEtCl<sub>2</sub> / AlCl<sub>3</sub> mixtures is the most favorable. Catalytic activity of nickel precursors was found to be higher due to the more acidic nature of these ionic liquids compared to [BMIM]Cl / AlEtCl<sub>2</sub>. [24]

When an IL containing AlEtCl<sub>2</sub> is contacted with a hydrocarbon layer, the dissociation equilibrium of polynuclear chloroethylaluminum anions is shifted to the formation of lower nuclear chloroaluminum anions and neutral chloroethylaluminum compounds (Eqs 5, 6). Because of the total miscibility of the latter aluminum derivatives and hydrocarbons, ethylaluminum species are leached into the organic phase and this leads to a change in the composition of the ionic liquid phase. [24] The extraction process, as well as the nature of the alkylaluminum species formed in various chloroaluminate ILs was investigated in detail by Gilbert *et al.* by Raman spectroscopy [37] in order to optimize acidity and catalytic activity of the system as well as to minimize the loss of AlEtCl<sub>2</sub>.



Ni salts (such as NiF<sub>2</sub> [25]), neutral (**1** (Figure 7) [23, 34], **2** [35], **3** [33, 34], **4** [34]) and cationic Ni-complexes ([Ni(MeCN)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> [25-27, 32], ([Ni(MeCN)<sub>6</sub>][AlCl<sub>4</sub>]<sub>2</sub>, ([Ni(MeCN)<sub>6</sub>][ZnCl<sub>4</sub>] [27]) as well as preformed (*e. g.* NiCl<sub>2</sub>(P(*i*-Pr)<sub>3</sub>)<sub>2</sub> (**5**) [23, 24], NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**6**) [22], NiCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> (**7**) [25]) or *in situ* produced Ni-phosphine complexes (*e. g.* NiCl<sub>2</sub>+PBu<sub>3</sub>, NiCl<sub>2</sub>+PPh<sub>3</sub>, NiCl<sub>2</sub>+PCy<sub>3</sub> [28])

and Ni-carbene complexes (8) [30] were found to be suitable catalyst precursors in chloroaluminate ILs (Table 4).

Various ligands/additives were found to affect greatly the activity and/or selectivity of the catalytic systems.

A decisive effect of the counter-anion of cationic Ni-complexes on the catalytic activity was observed. [27] Precursors with  $[\text{ZnCl}_4]^{2-}$  and  $[\text{AlCl}_4]^-$  anions led to enhanced catalytic activity (TOF:  $6480 \text{ h}^{-1}$ ) compared to  $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$  (TOF:  $2412 \text{ h}^{-1}$ ). This phenomenon was attributed to the highly reactive behavior of the  $[\text{BF}_4]^-$  ligand towards alkyl aluminum compounds. It can be assumed that a single active nickel hydride was formed in the ionic liquid, regardless of the precursor used, but in varying amounts depending on the counter ion for the different salts.

In case of  $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ , the use of  $\text{PCy}_3 \cdot \text{CS}_2$  as an additive led to considerably higher reaction rate (TOF:  $6840 \text{ h}^{-1}$ ) in oligomerization of 2-butene carried out in acidic ILs, than the addition of the phosphine  $\text{PCy}_3$  itself (TOF:  $3960 \text{ h}^{-1}$ ). [28] A systematic study of the effect of  $\text{PCy}_3 \cdot \text{CS}_2$  was carried out by de Souza. [29] According to the NMR investigations of different IL –  $\text{PCy}_3 \cdot \text{CS}_2$  systems, the improvement of catalytic activity is a consequence of a new anionic IL species, formed by the reaction of  $[\text{Al}_2\text{EtCl}_6]^-$  with the zwitterionic  $\text{PCy}_3 \cdot \text{CS}_2$ , that is able to coordinate to the nickel center and has a strong electron-withdrawing effect on the metal.

Various Ni-carbene complexes (8, Figure 7) were found to be more active catalysts of 1-butene oligomerization (with TOFs  $3820 \text{ h}^{-1} - 7020 \text{ h}^{-1}$ ) in chloroaluminate ILs than  $\text{NiCl}_2(\text{PCy}_3)_2$  (7, TOF= $2950 \text{ h}^{-1}$ ) under the same conditions. [30]

At the same time, because of a similar selectivity obtained in the presence of  $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ , a Ni-carbene complex and a nickel complex in an imidazolium IL with an imidazolium ion blocked with a methyl group in position 2, the active species are thought to be similar. As the formation of a Ni-carbene complex is not possible in the last case, it was concluded that the active catalyst was formed by the coordination of aluminum species to the nickel center in all cases. [26]

In the  $[\text{BMIM}]\text{Cl} / \text{AlEtCl}_2 / \text{AlCl}_3$  systems usually selective dimerization of ethene [25, 31, 38], propene [23, 24, 32] and butenes [26-29] could be observed due to the inhibition of cationic oligomerization/polymerization by the  $\text{AlEtCl}_2$  co-catalyst. [26]

It should be mentioned however, that by a proper change in the reaction temperature and alkylaluminum co-catalyst/Ni ratio, oligomerization of ethene could be shifted towards the formation of trimers. Both TOF values and  $C_6$  selectivity showed a curve with a maximum value with an increase in the  $\text{AlEt}_2\text{Cl}/\text{Ni}$  ratio. [22]

Oligomerization in acidic ILs was reported to lead to highly branched products. Besides, isomerization of both products and starting material was observed in most cases. For example, oligomerization of 1-butene and 2-butene led to the same product distribution, showing that isomerization was not a limiting step. [28]

Isomerization of the oligomerization products could be minimized by the proper choice of temperature and pressure during dimerization of propene: good selectivity for 1-hexene, up to 63%, could be achieved. [32]

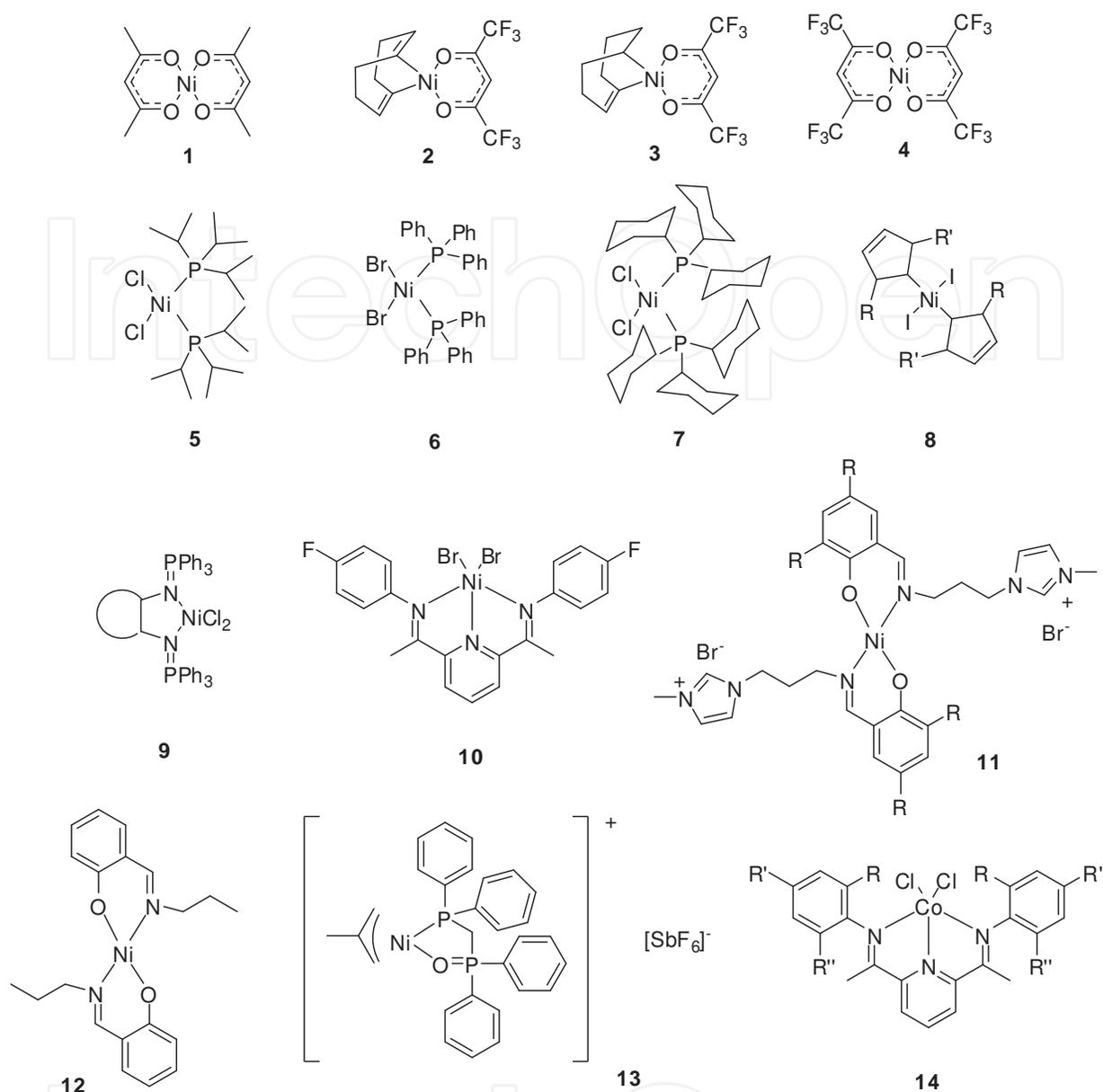
As linear C<sub>8</sub>-alkenes are highly desirable precursors of plasticizers, great efforts were made to develop a catalyst system producing linear oligomers. Complexes **2** and **3** (Figure 7), showing high selectivity in linear oligomerization in organic solvents, did not give satisfactory results in [BMPY]Cl / AlEt<sub>2</sub>Cl / AlCl<sub>3</sub> ILs. To avoid cationic side reactions, the use of buffered IL systems, consisting of [BMPY]Cl / AlCl<sub>3</sub> and an organic base, was investigated. [33, 35] The function of the base is to trap any free acidic species in the IL which may initiate cationic side reactions. Besides suitable basicity, the base should be non-coordinating with respect to the catalytically active nickel center. Depending on the nature of the base, 32-72% linear selectivity could be achieved in 1-butene oligomerization. Catalytic activity and selectivity was found to be optimal in the presence of *N*-methylpyrrole (TOF: 2100 h<sup>-1</sup>, linear selectivity: 51%) or chinoline (TOF: 1240 h<sup>-1</sup>, linear selectivity: 64%).

In oligomerization of propene, the same catalyst showed higher activity and dimer selectivity but lower linearity of the products in the buffered IL [EMIM]Cl / AlCl<sub>3</sub> / *N*-methylpyrrole than in toluene. [34] Selective dimerization was due to the 22 times lower solubility of the product hexenes in the IL than the starting material. The low linearity was attributed to ligand degradation in the presence of [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> anions present in the ionic liquid.

Highly selective dimerization of ethene, propene, 1-butene and 1-hexene could be carried out in the presence of **10** (Figure 7) in triphenylbismuth buffered chloroaluminate ILs, such as [MPYR][Al<sub>2</sub>Cl<sub>7</sub>]/ BiPh<sub>3</sub>. [39]

As chloroaluminate ILs promote isomerization of the double bond giving internal olefins as the main products, the possibility of the use of neutral ILs was also investigated. Hexafluorophosphate ILs with imidazolium cations were found to be suitable solvents for ethylene oligomerization with a cationic nickel-phosphine complex leading to 91-95% linear hexene selectivity, together with a 89-94% 1-hexene selectivity in the C<sub>6</sub> fraction. [40] The experiments showed enhanced activity in ILs (TOFs: 2058-12712 h<sup>-1</sup>) compared to the reaction in CH<sub>2</sub>Cl<sub>2</sub> (1852 h<sup>-1</sup>). Decreasing activity was observed with increasing alkyl chain length of the imidazolium cation. This phenomenon was explained by inhibition of the cationic nickel catalyst by the oligomers formed: oligomerization activity was reduced by both the monophasic reaction in CH<sub>2</sub>Cl<sub>2</sub> and increasing solubility of the products in the ILs with increasing alkyl chain length. Excellent 1-hexene selectivity is due to the low solubility of the oligomerization products in the IL. Since the primarily formed 1-olefins are quickly extracted into the organic layer, consecutive isomerization of these products at the Ni-center is suppressed. [41] A decisive negative effect of solvent impurities, such as chloride and water, on the outcome of the reaction was also revealed.

Active catalysts were generated from Ni(COD)<sub>2</sub> and the Brønsted acid, H(Et<sub>2</sub>O)<sub>2</sub>B[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub> in ILs such as [BMIM][NTf<sub>2</sub>] or [BMIM][SbF<sub>6</sub>]. [38] Contrary to organic solvents, the IL was able to stabilize and immobilize the active Ni species even in the absence of a coordinative ligand. In ethene oligomerization, high selectivity towards C<sub>4</sub>-C<sub>8</sub> olefins (above



**Figure 7.** Some transition metal complexes used in oligomerization reactions

90%), together with good activity, with TOFs between 1400-12000 h<sup>-1</sup>, were achieved in most cases. Selectivity for 1-butene was around 35% in the presence of IL/catalyst systems leading to C<sub>4</sub> products in good yields.

The main advantage of the use of the ionic liquid solvents in oligomerization is the possibility of catalyst reuse.

In butene dimerization the catalytic system, a [BMIM]Cl / AlCl<sub>3</sub> / AlEtCl<sub>2</sub> ionic liquid with an aluminum molar fraction of 0.57 and a cationic nickel complex, was reused for six times without any significant changes in the catalytic activity or selectivity. [22] The dimer distribution was almost constant throughout the catalytic runs. These indicate that the composition

of the catalytic species in the ionic liquid phase is not affected by the removal of the organic phase.

On the contrary, a drop of activity with constant selectivity was observed in the second run in chloroaluminate ILs composed of [BMIM]Cl / AlCl<sub>3</sub> / AlEtCl<sub>2</sub>=0.48/0.5/0.02. [26] At the same time, an increase in the TOFs from 5700 h<sup>-1</sup> to 6500 h<sup>-1</sup> and from 6100 h<sup>-1</sup> to 7600 h<sup>-1</sup> took place when the AlEtCl<sub>2</sub> content of the IL was raised to 5% and 10%, respectively. This shows that a minimal amount of co-catalyst is needed, probably to maintain a significant amount of active species through alkylation of the nickel species after the recycle.

Almost constant activity and selectivity could be ensured by the addition of a fresh supply of AlEt<sub>2</sub>Cl together with the *n*-heptane solvent after each run to the IL phase consisting of [BMIM]Cl / AlCl<sub>3</sub> / AlEt<sub>2</sub>Cl in ethene oligomerization. After three cycles, 98% of the original amount of nickel remained in the IL phase.[22]

The stability of the catalyst could be enhanced by the use of ligands with imidazolium tags. [42] Recycling experiments showed that bis-(salicylaldimine) Ni(II) complexes bearing imidazolium moieties in the side chains (**11**, Figure 7) could be recycled more efficiently, retaining their catalytic activity (with TOF values of 49 h<sup>-1</sup> – 41 h<sup>-1</sup>) at least in three cycles of ethene oligomerization. In contrast, activity of complex **12** dropped considerably upon reuse with TOFs of 48 h<sup>-1</sup> and 30 h<sup>-1</sup> in the first and second batch, respectively.

The catalytic system, the cationic Ni-complex (**13**, Figure 7) in [BMIM][PF<sub>6</sub>], was used successfully for biphasic oligomerization of ethene to higher  $\alpha$ -olefins. It was proved to be recyclable with little change in selectivity, although with somewhat lower activity. [40] The drop of TOF from 12712 h<sup>-1</sup> to 7952 h<sup>-1</sup> in the third run was attributed to the practical problem of quantitative transfer of the IL – catalyst mixture back into the autoclave under completely inert conditions.

Good results of catalyst reuse were obtained in ethene oligomerization in the presence of a catalyst generated from a Ni(0) complex and a Brønsted acid in [BMIM][SbF<sub>6</sub>]. [38]

The use of the IL solvent makes it possible to carry out the oligomerization reaction in a continuous mode. A loop reactor was designed where the biphasic reaction mixture was circulated by a pump with high flow rates. [33] Two static mixers in the reactor loop provided an efficient dispersion of the ionic catalyst solution in the organic phase. The product was separated from the IL/catalyst mixture with a gravity separator integrated in the reactor loop. After 3 h reaction time the [BMIM]Cl / AlCl<sub>3</sub> / N-methylpyrrole / **3** catalytic system showed good activity (TOF=2700 h<sup>-1</sup>) and selectivity (selectivity to C<sub>8</sub>-product >98%, selectivity to linear C<sub>8</sub>-product=52%).

## 5.2. Oligomerization with other transition metal catalysts

To avoid high carbon–carbon double bond isomerization rate, observed for nickel-catalyzed reactions, oligomerization catalysts based on other transition metals have also been tested (Table 4).

Cationic complexes of iron and cobalt,  $[\text{Fe}(\text{MeCN})_6][\text{BF}_4]_2$  and  $[\text{Co}(\text{MeCN})_6][\text{BF}_4]_2$ , showed catalytic activities *ca.* one order of magnitude lower in chloroaluminate ILs than the analogous nickel catalyst in ethene oligomerization. [43] At the same time, they exerted higher dimer selectivity (in the range of 79-100% for iron and 66-99% for cobalt) than the nickel derivative (43-68%) and excellent selectivity for 1-butene (up to 100% and 99% within the dimer fraction for the iron and cobalt complex, respectively.)  $\text{FeCl}_2$  and  $\text{CoCl}_2$  turned out to be more active but the absence of ligands resulted in considerably lower selectivity to  $\alpha$ -olefins.

Similarly to the nickel-catalyzed reactions, the addition of the ionic liquid greatly increased catalytic activity of the cationic complexes. Also, systems with more acidic co-catalysts, such as  $\text{AlEtCl}_2$  and  $\text{AlEt}_2\text{Cl}$ , showed higher activity than  $\text{AlEt}_3$  or methylaluminoxane.

Cyclodimerization of 1,3-butadiene, producing 4-vinyl-1-cyclohexene, was carried out in  $[\text{BMIM}][\text{BF}_4]$  in the presence of the catalyst precursor  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  and a reducing agent, such as Zn or  $\text{AlEtCl}_2$ . [44] In the latter case the conversion and turnover frequencies were similar to those obtained using Zn as reducing agent, but formation of some linear oligomers was observed. The use of the IL solvent greatly enhanced catalytic activity: the TOF achieved in the two-phase system ( $1404 \text{ h}^{-1}$ ) was higher than that under homogeneous conditions ( $253 \text{ h}^{-1}$ ). The catalytic system could be recovered and used in three successive experiments without any loss in the catalytic activity or selectivity.

Bis(imino)pyridine cobalt (II) catalysts (**14**, Figure 7) activated by methylaluminoxane were also found to be active in ethene oligomerization in chloroaluminate ILs. [45] They showed activities for ethene conversion in the range of  $4000\text{--}15300 \text{ h}^{-1}$ . The presence of electron withdrawing groups in the ligands, such as  $\text{CF}_3$  and F, Cl or Br, enhanced catalytic activity. The catalysts exhibited high selectivity (above 90%) for the dimerization of ethene. The major product was 1-butene for all the catalysts.

Tungsten complexes, generally applied to induce metathesis reactions, could also be used for the dimerization of ethene in chloroaluminate ILs. [46] The tungsten-imido complex  $\text{Cl}_2\text{W}=\text{NPh}(\text{PMe}_3)_3$  was found to be an active catalyst in slightly acidic  $[\text{BMIM}]\text{Cl} / \text{AlCl}_3$  even without the addition of  $\text{AlEtCl}_2$ . At the same time, the presence of the alkylaluminum co-catalyst was necessary in propene dimerization with the  $\text{Cl}_4\text{W}=\text{NPh}$  catalyst. In the latter case, contrary to the experiment starting from the phosphine complex, some leaching of the tungsten species to the organic phase was observed.

Palladium — Lewis acid systems, such as  $\text{Pd}(\text{OAc})_2/\text{Cu}(\text{OTf})_2$  and  $\text{Pd}(\text{OAc})_2/\text{In}(\text{OTf})_3$  were found to be very efficient catalysts for the selective dimerization of styrene to 1,3-diphenyl-1-butene in  $[\text{BMIM}][\text{PF}_6]$ . [47] Linear dimerization of 1,3-butadiene was achieved with  $\text{PdCl}_2$  in  $[\text{BMIM}][\text{BF}_4]$  and  $[\text{BMIM}][\text{PF}_6]$ . [48] Butadiene conversion was significantly higher in ILs than under homogeneous conditions. According to atomic absorption analysis, the palladium complex was almost completely retained in the ionic phase.

alkene	catalyst <sup>a</sup>	ionic liquid	reference
<b>oligomerization with Ni catalysts</b>			
ethene	NiF <sub>2</sub> , NiCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub> ( <b>7</b> ), [Ni(MeCN) <sub>6</sub> ][BF <sub>4</sub> ] <sub>2</sub>	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	25
ethene	NiBr <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ( <b>6</b> )	[BMIM]Cl / AlEt <sub>2</sub> Cl / AlCl <sub>3</sub>	22
ethene	<b>9</b>	[BMIM]Cl / AlEt <sub>2</sub> Cl / AlCl <sub>3</sub>	31
ethene	<b>11, 12</b>	[BMIM]Cl / AlEt <sub>2</sub> Cl / AlCl <sub>3</sub>	42
ethene	Ni(COD) <sub>2</sub> / H(Et <sub>2</sub> O) <sub>2</sub> B[3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>4</sub>	[BMIM][NTf <sub>2</sub> ], [BMIM][SbF <sub>6</sub> ]	38
ethene	<b>13</b>	[BMIM][PF <sub>6</sub> ]	40, 41
propene	[Ni(MeCN) <sub>6</sub> ][BF <sub>4</sub> ] <sub>2</sub>	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	32
propene	NiCl <sub>2</sub> (P( <i>i</i> -Pr) <sub>3</sub> ) <sub>2</sub> ( <b>5</b> )	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	23, 24
	NiCl <sub>2</sub> (PBU <sub>3</sub> ) <sub>2</sub>		
	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>		
	NiCl <sub>2</sub> (PBz <sub>3</sub> ) <sub>2</sub>		
propene	NiCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub> ( <b>7</b> )		
propene	Ni(acac) <sub>2</sub> ( <b>1</b> )	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	23
propene	<b>8</b>	[BMIM]Cl / <i>N</i> -methylpyrrole / AlCl <sub>3</sub>	30
propene	Ni(acac) <sub>2</sub> ( <b>1</b> ), <b>3, 4</b>	[EMIM]Cl / <i>N</i> -methylpyrrole / AlCl <sub>3</sub>	34
propene	<b>10</b>	[MPYR][Al <sub>2</sub> Cl <sub>7</sub> ] / BiPh <sub>3</sub>	39
1-butene	[Ni(MeCN) <sub>6</sub> ][BF <sub>4</sub> ] <sub>2</sub> Ni(MeCN) <sub>6</sub> [AlCl <sub>4</sub> ] <sub>2</sub> , [Ni(MeCN) <sub>6</sub> ][ZnCl <sub>4</sub> ]	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	26, 27
1-butene	[Ni(MeCN) <sub>6</sub> ][BF <sub>4</sub> ] <sub>2</sub> + PCy <sub>3</sub> CS <sub>2</sub>	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	29
1-butene, 2-butene	NiCl <sub>2</sub> + PBU <sub>3</sub> , NiCl <sub>2</sub> + PPh <sub>3</sub> , NiCl <sub>2</sub> + PCy <sub>3</sub> , NiCl <sub>2</sub> + PCy <sub>3</sub> CS <sub>2</sub>	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	28
1-butene	<b>8</b>	[BMIM]Cl / <i>N</i> -methylpyrrole / AlCl <sub>3</sub>	30
1-butene	<b>3</b>	[BMPY]Cl / LiCl / AlCl <sub>3</sub> [BMPY]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub> [BMPY]Cl / <i>N</i> -methylpyrrole / AlCl <sub>3</sub> [BMIM]Cl / <i>N</i> -methylpyrrole / AlCl <sub>3</sub>	33
1-butene	<b>2</b>	[BMPY]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub> [BMPY]Cl / <i>N</i> -methylpyrrol / AlCl <sub>3</sub>	35
<b>oligomerization with other transition metal catalysts</b>			
ethene	[Fe(MeCN) <sub>6</sub> ][BF <sub>4</sub> ] <sub>2</sub>	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	43

alkene	catalyst <sup>a</sup>	ionic liquid	reference
		[BMIM]Cl / AlEt <sub>2</sub> Cl / AlCl <sub>3</sub> [BMIM]Cl / AlEt <sub>3</sub> / AlCl <sub>3</sub> [BMIM]Cl / MAO / AlCl <sub>3</sub>	
1,3-butadiene	[Fe(NO) <sub>2</sub> Cl] <sub>2</sub> / Zn or AlEtCl <sub>2</sub>	[BMIM][BF <sub>4</sub> ]	44
ethene	[Co(MeCN) <sub>6</sub> ][BF <sub>4</sub> ] <sub>2</sub>	[[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub> [BMIM]Cl / AlEt <sub>2</sub> Cl / AlCl <sub>3</sub> [BMIM]Cl / AlEt <sub>3</sub> / AlCl <sub>3</sub> [BMIM]Cl / MAO / AlCl <sub>3</sub>	43
ethene	<b>14</b>	[BMIM]Cl / MAO / AlCl <sub>3</sub>	45
ethene	Cl <sub>2</sub> W=NPh(PMe <sub>3</sub> ) <sub>3</sub>	[BMIM]Cl / AlCl <sub>3</sub>	46
propene	Cl <sub>4</sub> W=NPh	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	46
styrene	Pd(OAc) <sub>2</sub> /Cu(OTf) <sub>2</sub> Pd(OAc) <sub>2</sub> /In(OTf) <sub>3</sub>	[BMIM][PF <sub>6</sub> ]	47
1,3-butadiene	PdCl <sub>2</sub>	[BMIM][BF <sub>4</sub> ] [BMIM][PF <sub>6</sub> ]	48

<sup>a</sup>: for structures of catalysts **1-14** see Figure 7.

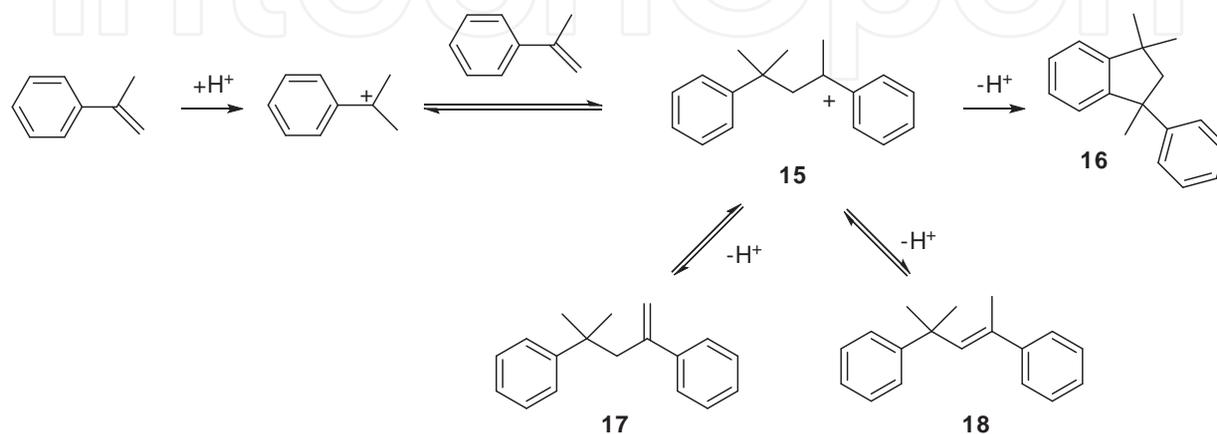
**Table 4.** Oligomerization of alkenes in ILs with transition metal catalysts

### 5.3. The use of ILs as solvents in acid-catalyzed oligomerizations

Air-stable nonchloroaluminate ILs can be used as solvents for catalytic amounts of protic acids (Table 5). In this case the IL is used to immobilize the acid catalyst and to ensure a biphasic reaction. The acidity of the system can be tuned by the nature of the acid/IL composition. The acidity level of these systems can be evaluated by the determination of the Hammett acidity functions using UV-Visible spectroscopy. [49, 50] (For a review, see [51].) These results were in good agreement with the catalytic data obtained for oligomerization of isobutene in most ILs except for [BMIM][NTf<sub>2</sub>]. [52] The choice of the anion of the IL and the nature and concentration of the Brønsted acid were the main factors influencing catalytic performance. Although excellent conversions were obtained with HNTf<sub>2</sub> or HOTf, dimer selectivity remained moderate and trimers were formed in a large amount. Under the same acid concentrations, no reaction was observed either in organic solvents, such as heptane, or in water. Due to the solvating effect of water with respect to the proton, even addition of water to an IL/acid system decreased considerably the acidity level of the proton.

The catalytic system composed of [HMIM][BF<sub>4</sub>] and HBF<sub>4</sub> showed high catalytic activity in dimerization of  $\alpha$ -methylstyrene (Scheme 7) to produce 4-methyl-2,4-diphenyl-1-pentene (**17**) at 60°C. [53] The catalyst could be reused in four cycles without a loss of activity or selectivity. HBF<sub>4</sub> alone was found to be a considerably less active catalyst leading to a 6% conversion of  $\alpha$ -methylstyrene under identical conditions. The IL [HMIM][BF<sub>4</sub>] exerted no catalytic activity

without the addition of an acid. The use of ILs with other anions or the addition of other acids than  $\text{HBF}_4$  led to lower activity and/or lower selectivity. At the same time, the cation of the IL had no significant influence,  $[\text{BMIM}][\text{BF}_4]-\text{HBF}_4$ ,  $[\text{MIM}][\text{BF}_4]-\text{HBF}_4$  and  $[\text{EMIM}][\text{BF}_4]-\text{HBF}_4$  were similarly suitable compositions. The reaction temperature had a great effect on the selectivity of the reaction, at  $120\text{ }^\circ\text{C}$  selective formation of **16** was observed.



**Scheme 7.** Oligomerization of  $\alpha$ -methylstyrene

alkene	acidic catalyst	ionic liquid	reference
isobutene	$\text{HNTf}_2$	$[\text{BMIM}][\text{NTf}_2]$ $[\text{BMIM}][\text{OTf}]$ $[\text{BMIM}][\text{PF}_6]$ $[\text{BMIM}][\text{BF}_4]$ $[\text{BMIM}][\text{SbF}_6]$	52
isobutene	$\text{HOTf}$	$[\text{BMIM}][\text{NTf}_2]$	52
isobutene	$\text{CH}_3\text{SO}_3\text{H}$	$[\text{BMIM}][\text{NTf}_2]$	52
isobutene	$\text{CF}_3\text{CO}_2\text{H}$	$[\text{BMIM}][\text{NTf}_2]$	52
$\alpha$ -methylstyrene	$\text{HBF}_4$	$[\text{HMIM}][\text{BF}_4]$ $[\text{BMIM}][\text{BF}_4]$ $[\text{EMIM}][\text{BF}_4]$ $[\text{MIM}][\text{BF}_4]$	53

**Table 5.** Acid catalyzed oligomerization in ILs

## 6. Ionic liquids as catalysts

The first example for an IL catalyzed oligomerization of low molecular weight olefins was described in 1993 (Table 6). [54] Ethene or propene were converted to a mixture of oligomeric saturated and unsaturated hydrocarbons. The [BMIM]Cl / AlCl<sub>3</sub> system was shown to give unsaturated C<sub>4</sub>-C<sub>6</sub> hydrocarbons with better selectivity than the more acidic [BPY]Cl / AlCl<sub>3</sub>.

As it was described in the previous section, the formation of highly viscous oligomeric products were found to be formed in acidic chloroaluminate ILs even in the absence of a nickel catalyst [23, 26] but according to the reports, this reaction could be suppressed in the presence of the alkylaluminum co-catalyst. At the same time, Stenzel et al. reported on the oligomerization of 1-alkenes in the IL with a composition of [BMIM]Cl / AlCl<sub>3</sub> / AlEtCl<sub>2</sub>=1/1.1/0.1. [55] The reaction was much slower than the transition metal catalyzed oligomerization: 67% ethene conversion was achieved in 16h at 60 °C. The total yield of oligomers decreased with increasing chain length of the monomer (to 7% in the oligomerization of 1-hexene).

Oligomerization of 1-hexene, [56, 57] 1-octene [58] and 1-decene [58] led to oligoalkylnaphtenic oils in chloroaluminate ionic liquids, such as [Et<sub>3</sub>NH]Cl / AlCl<sub>3</sub>, [PY]Cl / AlCl<sub>3</sub> and 2,6-bis(morpholinylethyl)-4-methylphenol/AlCl<sub>3</sub>. The products were formed via an oligomerization – cyclization reaction sequence. The introduction of a titanium containing modifier into the chloroaluminate IL leads to the formation of new catalytic centers that mediate the oligomerization process toward the formation of oligomers with a higher molecular mass. [56]

Chloroaluminate ionic liquids are extremely moisture-sensitive and hydrolyze to release hydrogen chloride in contact with traces of water. Besides, they promote not only cationic oligomerization but also isomerization. As a consequence, the catalytic activity of chloroferrate(III)-[59] and chlorogallate(III) ILs [60], less sensitive to hydrolysis, were also tested.

Acidic compositions of [Et<sub>3</sub>NH]Cl / FeCl<sub>3</sub> and [C<sub>13</sub>H<sub>22</sub>N]Cl / FeCl<sub>3</sub> showed high activity in isobutene oligomerization leading to a mixture of diisobutene and triisobutene with high selectivity. [59] The conversion of isobutene increased with increasing reaction temperature, but at high temperature cracking reactions occurred. The addition of CuCl to iron(III) chloride ionic liquids increased catalytic activity and the selectivity for diisobutene plus triisobutene up to 90 % using a composition of CuCl / [Et<sub>3</sub>NH]Cl / FeCl<sub>3</sub>=0.25/1/1.5.

[EMIM][Ga<sub>2</sub>Cl<sub>7</sub>] was successfully used in the oligomerization of 1-pentene to produce a C<sub>20</sub>-C<sub>50</sub> fraction, that can be used as a base for synthetic automotive lubricants, with high selectivity. [60]

A considerably different activity and selectivity of chloroaluminate and chloroferrate ILs were observed in oligomerization of  $\alpha$ -methylstyrene (Scheme 7). [61] With [Et<sub>3</sub>NH]Cl / 2AlCl<sub>3</sub> 100% conversion was achieved in 5 minutes. The selectivity for 1,1,3-trimethyl-3-phenylindan (**16**) was as high as about 97% in the absence of organic solvents. [Et<sub>3</sub>NH]Cl / 2FeCl<sub>3</sub>, [BMIM]Br / 2AlCl<sub>3</sub>, [BMIM]Br / 2FeCl<sub>3</sub> turned out to be similarly active but less selective catalysts producing 22-32% trimers as side products. In [BMIM]Cl / 2AlCl<sub>3</sub> complete selectivity towards **16** was observed. [53] The high activity of the chloroaluminate ionic liquid was attributed to the strong

alkene	ionic liquid	reference
ethene	[BMIM]Cl / AlCl <sub>3</sub> [BPY]Cl / AlCl <sub>3</sub>	54
ethene	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	55
propene	[BMIM]Cl / AlCl <sub>3</sub> [BPY]Cl / AlCl <sub>3</sub>	54
propene	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	55
1-butene	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	55
isobutene	[Et <sub>3</sub> NH]Cl / FeCl <sub>3</sub> [C <sub>13</sub> H <sub>22</sub> N]Cl / FeCl <sub>3</sub> [Et <sub>3</sub> NH]Cl / FeCl <sub>3</sub> / CuCl	59
isobutene	[MIMBs][OTf] [HIMBs][OTf]	64
isobutene	[MIMBs][OTf] / [BMIM][OTf]	52
1-pentene	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	55
1-pentene	[EMIM][Ga <sub>2</sub> Cl <sub>7</sub> ]	60
1-hexene	[BMIM]Cl / AlEtCl <sub>2</sub> / AlCl <sub>3</sub>	55
1-hexene	[Et <sub>3</sub> NH]Cl / AlCl <sub>3</sub> [PY]Cl / AlCl <sub>3</sub> 2,6-bis(morpholinylethyl)-4-methylphenol/AlCl <sub>3</sub> 2,6-bis(morpholinylethyl)-4-methylphenol/TiCl <sub>4</sub>	56, 57
1-octene	[Et <sub>3</sub> NH]Cl / AlCl <sub>3</sub> [PY]Cl / AlCl <sub>3</sub>	58
1-decene	[Et <sub>3</sub> NH]Cl / AlCl <sub>3</sub> [PY]Cl / AlCl <sub>3</sub>	58
α-methylstyrene	[BMIM]Cl / AlCl <sub>3</sub>	53
α-methylstyrene	[Et <sub>3</sub> NH]Cl / AlCl <sub>3</sub> [Et <sub>3</sub> NH]Cl / FeCl <sub>3</sub> [BMIM]Br / AlCl <sub>3</sub> [BMIM]Br / FeCl <sub>3</sub>	61
α-methylstyrene	[MIM][BF <sub>4</sub> ]	62
α-methylstyrene	[MIMBs][OTf] [HIMBs][OTf]	64

**Table 6.** Oligomerization of alkenes with IL catalysts

Lewis acid, as well as superacidic protons, existing in the system due to the release of hydrochloric acid in the presence of trace amounts of water (see Eq. 4).

Stabilization of the intermediate carbenium ion (**15**, Scheme 7) by the IL with great polarity may make it possible for the positively charged carbon to attack the aromatic ring leading to the cyclodimer **16**. At the same time, in tertiary-amylalcohol as solvent,  $[\text{Et}_3\text{NH}]\text{Cl} / 2\text{FeCl}_3$  oligomerizes  $\alpha$ -methylstyrene to unsaturated dimer **17** with high selectivity. Interestingly, activity of  $[\text{Et}_3\text{NH}]\text{Cl} / 2\text{AlCl}_3$  was much lower under these conditions, probably due to the better solvation of  $\text{Al}^{3+}$  than that of  $\text{Fe}^{3+}$  in the organic solvent.

The Brønsted acidic IL,  $[\text{MIM}][\text{BF}_4]$  was shown to catalyze selective dimerization of  $\alpha$ -methylstyrene, without the addition of an acidic co-catalyst. [62] This can be explained by the higher acidity of  $[\text{MIM}][\text{BF}_4]$  compared to dialkylimidazolium ILs. [63] In the dimerization reaction, a great temperature dependence on the selectivity was observed: at 60 °C 4-methyl-2,4-diphenyl-1-pentene (**17**) was formed with 93% selectivity at 92% conversion of the substrate, while indan **16** could be obtained with 100% selectivity when the reaction temperature was increased to 170 °C. The ionic liquid was successfully recycled six times.

Other Brønsted acidic ILs, consisting of imidazolium cations with alkane sulfonic acid side chains, were found to be equivalently active but less selective catalysts in the dimerization of  $\alpha$ -methylstyrene. [64] At the same time, in oligomerization of isobutene, 68% and 94 % conversion and 99% selectivity to  $\text{C}_{8+}\text{C}_{12}$  products, starting material for the production of high-octane gasoline blending components, could be achieved with  $[\text{MIMBs}][\text{OTf}]$  and  $[\text{HIMBs}][\text{OTf}]$  (Figure 6), respectively. The selectivity of the reaction was greatly dependent on the length of the side chain of the imidazolium cation. The use of an ionic liquid with smaller side chain led to higher selectivity for dimeric products. The increase in the catalytic activity of  $[\text{HIMBs}][\text{OTf}]$  was attributed to the higher solubility of isobutene in this IL because of the greater lipophilicity of the imidazolium cation with the longer alkyl side chain. It should be mentioned that using 1-alkenes as substrates, isomerization, instead of oligomerization, was found to be the main reaction.

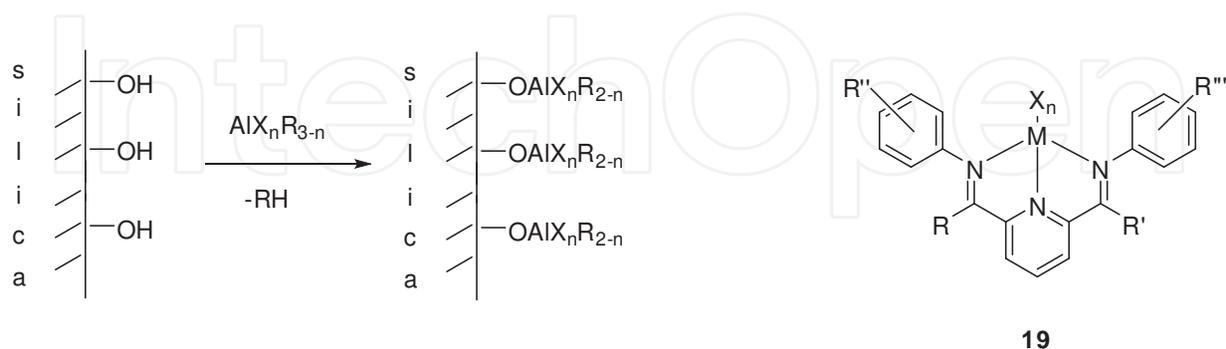
A Brønsted acidic IL could also be used in catalytic amounts in a neutral IL as solvent.  $[\text{MIMBs}][\text{OTf}]$  (Figure 6) was proved to be a more efficient acidic catalyst for isobutene dimerization in  $[\text{BMIM}][\text{OTf}]$  solvent than  $\text{HNTf}_2$  or  $\text{HOTf}$  regarding dimer selectivity (up to 88 % at 70% isobutene conversion). [52] The  $[\text{MIMBs}][\text{OTf}] / [\text{BMIM}][\text{OTf}]$  mixture retained its activity and selectivity in ten subsequent cycles.

## 7. Supported catalysts based on ILs

Despite the several advantages of ILs discussed in the previous sections, they also have some drawbacks including the difficulties in handling because of the high viscosity of some ILs and the problems for application in fixed bed reactors. Also, biphasic IL – organic systems require large amounts of the expensive ILs, which hinders industrial applications. These difficulties can be overcome by the use of supported ionic liquid phases (SILPs) prepared by the immobilization of ILs on solid supports. [65]

Supported versions of the transition metal catalyzed processes, easy to use in a continuous mode reactor, were described. A buffered IL immobilized on a support material together with

an organometallic complex of the type **19** (Figure 8) was used in selective dimerization reactions. The OH groups of the support were modified with an aluminum halide or alkylaluminum halide (Figure 8). The immobilized buffered catalyst was formed by mixing the organometallic catalyst, the IL composition of [BMIM]Cl/AlCl<sub>3</sub> and the coated support. The methodology was successfully used for the dimerization of propene in a fixed bed reactor. [66]



**Figure 8.** Modification of silica with an aluminum halide/alkylaluminum halide, and complex **19** (M=Ni, Fe, Co, Ti, V) used as the catalyst precursor

Immobilization of metallocene catalysts for the same reaction was achieved by similar methodology. [67]

Silica-supported SO<sub>3</sub>H-functionalized IL catalysts were used in the oligomerization of isobutene. [68] The catalysts were obtained by impregnation of silica supports with Brønsted acidic ILs with [MIMBs]<sup>+</sup> or [BIMBs]<sup>+</sup> cations resulting in the formation of a solid material. It was shown that various factors, such as the properties and pretreatment of the solid support, the choice of cation and anion, as well as the reaction time and temperature affected the outcome of the reaction considerably. Oligomerization of isobutene, carried out at 60 °C, led to the formation of C<sub>8</sub> products with very good selectivity in each case. An increase in the temperature and/or reaction time led to an increase in the ratios of higher oligomers with selectivities for C<sub>12</sub>+C<sub>16</sub> products up to 85%. The catalysts comprising a trifluoromethanesulfonate anion could be reused several times without loss of activity. Total catalyst leaching of eight successive runs was 2.0% of the original load. At the same time, a quick inactivation of the catalysts obtained from ILs with hydrogensulfate anions was observed.

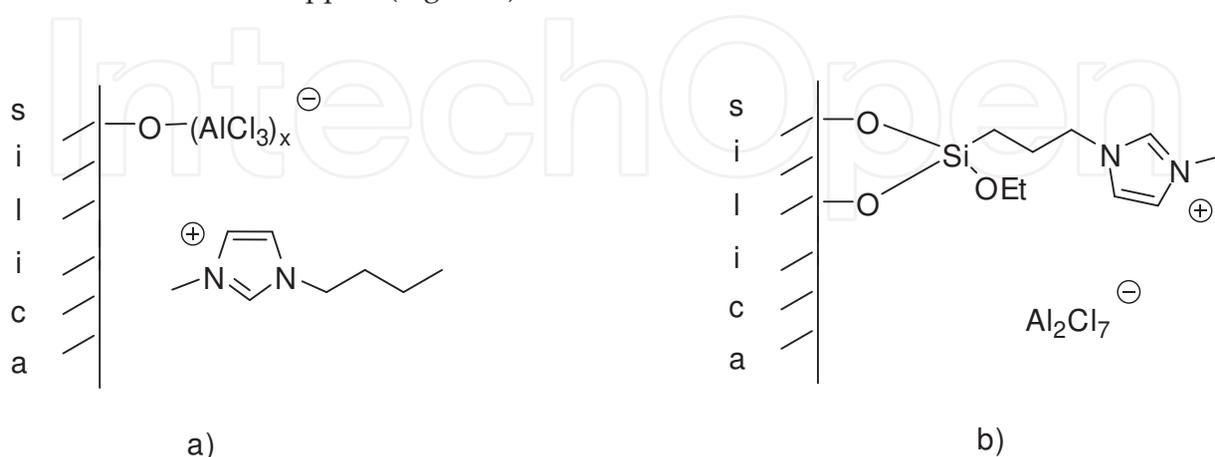
The TON and TOF values of the SILP catalysts were found to be ten times higher than those of the same ILs. When using the SILP catalysts, a smaller amount of the relatively expensive ionic liquid was sufficient for the reaction. The mass transport into the ionic liquid phase can be rate limiting due to the high viscosity of the ILs. This drawback can be circumvented by dispersing the ILs on support materials. Furthermore, the solid catalysts are easier to handle than the ionic liquids themselves, so separation and recovery of even small amounts of catalysts are simple.

Both mesoporous and microporous silica materials were used as solid supports. [69] A close relationship between catalytic activity and catalyst morphology was observed. Silica with mesoporous structure was able to adsorb a higher amount of the IL and produced SILP

materials with higher catalytic activity at identical catalyst loadings. The formation of a stable film was a prerequisite for an unvarying selectivity of the catalyst, so impregnation at a high temperature was necessary to obtain a suitable composition, especially in case of microporous support materials.

As it could be expected, immobilization of the IL led to a loss of the BET surface of the supports. From the experimental data of the nitrogen adsorption/desorption isotherms of the supports and the solid catalysts, it could be concluded that the pores of mesoporous supports retained their shape during the catalyst preparation process, although the total pore volume values decreased because of the active IL film on the wall of the pores. On the other hand, the microporous supports contained narrow shaped pores that became almost totally filled with IL film during the catalyst preparation. The diffusion of isobutene to the micropores was blocked by the IL that filled the pore, so the contact surface between the IL phase and the organic phase was lower than that of SILP catalysts with mesopores. Also, acid capacity of microporous material was found to be lower, in accordance with the different amounts of adsorbed ionic liquid. Lower contact surface and lower acidity resulted in lower catalytic activity. At the same time, using a proper pretreatment, a stable catalyst with excellent  $C_{12}$  selectivity, exceeding even that of the mesoporous material, could be obtained with ILs supported on microporous silica.

Supported chloroaluminate ILs were used for the trimerization of isobutene in a feed containing  $C_4$  mixture. [70] Both the support and immobilization methodology were found to play a crucial role in the reaction. Catalysts obtained by mixing the IL with the silica support showed excellent oligomerization activity. At the same time, ILs immobilized on glass or molecular sieves induced only isobutane/butene alkylation. Exclusive alkylation took place also in the presence of catalysts prepared by grafting the IL on the silica. According to  $^{29}\text{Si}$  CP/MAS NMR measurements, in the latter case a covalent bond was formed between the cation and the support. On the contrary, the spectrum of the catalyst with oligomerization activity indicated the formation of a covalent bond between the anion of the Lewis acid and the silanol group on the surface of the support (Figure 9).



**Figure 9.** Structures of immobilized IL on silica support prepared by different methods (a) by mixing the IL and the silica support, b) by grafting)

[BMIM]Cl was used as a template during the preparation of a  $\beta$ -zeolite, a support for nickel- $\beta$ -diimine catalysts that were highly active in oligomerization of ethene. [71] The high regularity of the microspherical agglomerates, obtained during the preparation of the support, was attributed to the formation of micellar aggregates due to the IL. The nickel complex incorporated into the  $\beta$ -zeolite framework showed higher activity, higher  $C_4$  (up to 93.8%) and 1-butene selectivities (85.7% of the  $C_4$  fraction) than the homogeneous catalyst. The  $\beta$ -zeolite structure was found to work as a shape-selective support that inhibited re-coordination of 1-butene, thereby preventing isomerization and growth of the oligomer chain.

## 8. Industrial processes and patents based on the use of ionic liquids

Some of the catalyst compositions, described in the previous sections, were also patented.

Researchers of the Institut Français du Pétrole (IFP) described the use of chloroaluminate ILs, composed of imidazolium or pyridinium halides and  $AlCl_3$  as solvents for nickel catalyzed oligomerizations as early as 1987. [21] An improvement of the system by the addition of an alkylaluminum chloride co-catalyst, [72] and the use of an aromatic hydrocarbon to control the acidity of the system were patented soon afterwards. [73]

In 1998, an industrial process based on chloroaluminate ILs and nickel catalysts, known as the Difasol™ technology, was commercialized. It can be considered as a biphasic variant of the original homogeneous Dimersol X™ process that converts butenes to dimers. [19] As conversion is dependent on the initial concentration of butenes, the use of the latter technology is limited to  $C_4$  feed with a minimum of 60% butene content. The liquid-liquid biphasic process can convert dilute feeds and can produce dimers with high selectivity that does not depend on conversion due to the low solubility of the product dimers in the ionic phase. The Difasol system is ideally suited for use as the finishing reaction section for a conventional Dimersol unit and importantly, it can be fitted into existing Dimersol plants to give improved yields and lower catalyst consumption. The sequence increases the relative octene gain by 22-41% over the traditional single process. [74] By the use of an appropriate ligand with a coordinating nitrogen, the catalyst system containing a zerovalent nickel complex, an acid and the IL can be tuned to obtain either dimers, oligomers or polymers with good selectivity. [75]

BP Chemicals also patented catalytic systems containing nickel-complexes in buffered ILs with a composition of  $R_nMCl_{3-n}$  or  $R_mM_2Cl_{6-m}$  (M: Al, Ga, B or Fe(III)), an organic halide and a weak base. [76]

Catalysts composed of a Lewis acid and an IL [77] as well as the catalytic activity of acidic chloroaluminate(III) and alkylchloroaluminate(III) ILs [78] in oligomerization of light olefins were patented in 1995. Using the latter system, the olefinic feedstock could simply be bubbled through the ionic liquid catalyst, or alternatively, in a batch process, the IL was injected into a charged autoclave. With the use of imidazolium ions with alkyl groups longer than  $C_5$ , the reaction could be pushed towards polymerization.

Good trimer selectivity was obtained in oligomerization of isobutene in the presence of chloroindate ILs. Catalysts with ILs supported on silica were also used efficiently. [79]

Synthesis of polyalphaolefins, starting from 1-decene or 1-dodecene, was described in imidazolium, pyridinium, phosphonium, ammonium or sulfonium halides combined with an aluminum- or gallium halide or alkylhalide. [80] A continuous mode of operation, using the same composition, was also patented by Chevron. [81] Not only the proper choice of the catalytic system but also the use of an appropriate operational mode is important to achieve optimal results. It was shown that the activity of the IL catalyst could be increased by emulsifying the IL with one or more liquid components. [82]

Efficient processes can be developed by the combination of oligomerization in ILs with other methodologies. An acidic IL catalyst consisting of an organic salt and a Lewis acid was used for the oligomerization of a light olefinic by-product fraction from a metallocene-catalyzed polyalphaolefin oligomerization process. [83]

Oligomerization of olefins present in the condensate recovered from the Fischer-Tropsch reactor can lead to high quality lube base oils. [84] However, the presence of oxygenates was found to interfere with the oligomerization of olefins catalyzed by Lewis acidic ILs. The amount of oxygenates could be reduced by contacting the feed with a hydrotreating catalyst prior to oligomerization. [85] The olefin stream formed by the Fischer-Tropsch synthesis and containing 1-alkenes with 5-18 carbon atoms could be converted into lubricating oils having a viscosity index of at least 120 and a pour point of -45 °C or less. [86]

Oligomerization of olefins together with an alkylation in the presence of isoparaffins could be carried out using the same IL catalysts. This may provide an efficient way to reduce the concentration of double bonds and at the same time to enhance the quality of the product. [87]

A Lewis acidic IL was supported on a porous solid and served as an adsorbent and activator for a Brønsted acid catalyst. The catalytic system was used in a fixed bed reactor, constructed for oligomerization or combined oligomerization /alkylation reactions. [88] In order to be able to respond to changing market demands, a process adjusting operational mode between two levels, a low level that favors the synthesis of C<sub>5+</sub> products boiling at 137.8 °C or below or another C<sub>5+</sub> product boiling above this temperature, was developed combining alkylation/oligomerization in ILs. [89]

## 9. Conclusions

The use of ILs in catalytic reactions is a quickly expanding area of chemical research that has a great potential for industrial applications. Oligomerization of alkenes with ILs is one of the most promising methodologies to be implemented as industrial processes, although until now only one example, the Difasol™ technology, exists. [19]

The results presented in the previous sections show that ILs can really be used efficiently either as solvents or catalysts in oligomerization reactions. Catalytic activity of transition metal

complexes was shown to be enhanced in ILs compared to organic solvents and ILs were proved to ensure easy product separation and efficient catalyst recycling. Technologies using ILs can convert not only pure alkenes but also process streams containing olefins to oligomers and can also be combined with other hydrocarbon conversion processes.

The effects of chloroaluminate ILs on nickel-catalyzed reactions are relatively well explored and from the investigations it can be concluded that a careful fine-tune of IL composition is necessary to obtain satisfactory results. However, in most cases little is known about the active transition metal species and the choice of the cations restricted mainly to imidazolium or pyridinium ions. There are still plenty of possibilities for the design of new IL compositions with better performance. This is even more true for ILs with oligomerization activity. To obtain an IL composition with optimal acidity, in order to achieve high conversion and at the same time to avoid polymerization or formation of higher oligomers, is a key issue in future research.

However, one of the main drawbacks that hinder industrial applications of ILs is the still high cost of these materials. In this respect, the use of supported catalysts opens new possibilities. Besides reducing the quantity of ILs necessary for the catalytic reactions, immobilization on solid supports makes it possible to use the catalysts in fixed bed reactors in continuous mode. At the same time, recent observations clearly show that compared to the non-immobilized IL catalysts, there are numerous other factors here that influence catalytic performance. Not only the IL composition but also the choice of the support material, porosity of the support and immobilization methodology affects catalytic activity and selectivity.

## Abbreviations

BIMBs: 1-(4-sulfobutyl)-3-butylimidazolium

BMIM: 1-butyl-3-methylimidazolium

BMPY: 1-butyl-4-methylpyridinium

BPY: 1-butyl-pyridinium

Bz: benzyl

Cy: cyclohexyl

EMIM: 1-ethyl-3-methylimidazolium

HIMBs: 1-(4-sulfobutyl)-3-hexylimidazolium

HMIM: 1-hexyl-3-methylimidazolium

IL: ionic liquid

MAO: methylaluminoxane

MIM: 1-methyl-3H-imidazolium

MIMBs: 1-(4-sulfobutyl)-3-methylimidazolium

MPYR: 1-methylpyrrolidinium

NTf<sub>2</sub>: bistrifluoromethylsulfonimide

OTf: trifluoromethanesulfonate

PAO: poly- $\alpha$ -olefin

PY: pyridinium

RON: research octane number

toe: tonne of oil equivalent

## Acknowledgements

The present work was funded by the project TÁMOP-4.2.2.A-11/1/KONV-2012-0071, realized with the support of the Hungarian Government and the European Union, with the co-funding of the European Social Fund.

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