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# Oligomerization of Ethylene Catalyzed by Iron and Cobalt in Organoaluminate Dialkylimidazolium Ionic Liquids

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**Abstract** Cationic iron and cobalt acetonitrile cationic complexes were prepared and used as catalyst precursors in catalytic ethylene oligomerization. The effects of temperature and the nature and effects of the co-catalysts were evaluated. The iron and cobalt catalysts are less active, giving turnover frequencies of 20,000 to 30,000 $h^{-1}$ while the corresponding nickel analogs exhibit turnover frequencies of 215,000 $h^{-1}$. The iron and cobalt catalysts were more selective for the synthesis of 1-butene, especially at lower temperatures, compared to the nickel catalyst.

**Keywords** Ethylene · Oligomerization · Iron · Cobalt · Organoaluminate · Ionic liquid

## 1 Introduction

Recent developments in the use of coordination compounds as catalysts for the synthesis of linear α-olefins were made possible by the suitable development of ligands and the use of different metals. The advances achieved in this field allow access to catalysts that permit selective dimerization [1–3], trimerization [4], tetramerization [5], and even specific oligomerization [6] of ethylene.

Although many types of oligomerization catalysts are known, the selective production of linear α-olefins, particularly those in the range of $C_6$–$C_{12}$, still present a great challenge. These systems pose several problems, including that of selectivity. The major difficulty is catalyst death due to deactivation during the separation of products from the catalyst. Some approaches have been developed to overcome this drawback. The most successful have been the chemical or physical immobilization of coordination compounds, allowing access to the advantages of heterogeneous catalysis, and the use of liquid–liquid biphasic catalysts, using ionic liquids as the immobilization phase for the transition metal catalysts.

Oligomerization reactions in which ionic liquids act as the immobilization phase have been studied extensively for homogeneous nickel catalysts. Aspects such as the influence of ionic liquid acidity, due to the variety of compositions that can be obtained in chloroaluminate ionic liquids [7–9], additives [10, 11], variations in ionic liquids [12, 13] and reactor design [14, 15] have been considered. Several oligomerization catalysts were evaluated in ionic liquids, with different organic moieties [8, 12, 13, 16–22] and different counter-anions in cationic coordination compounds [23].

Many experiments have been performed to find appropriate conditions for the selective synthesis of linear α-olefins. Nickel coordination compounds are still the most successfully used complexes for oligomerization reactions in ionic liquids [12], but their impact has been limited by the isomerization of the produced olefins [24]. We thus extended our studies of oligomerization reactions in ionic liquids to iron and cobalt catalysts for which several attractive descriptions have become available in recent years. To our knowledge, no studies have been published demonstrating the use of cobalt and iron catalysts for oligomerization in ionic liquids. With this goal, two cationic coordination compounds with structures very similar to known nickel analogs were prepared, and their catalytic

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behavior while changing the co-catalyst and reaction temperature was evaluated. Their results were compared with their nickel analogs, which have been well described in the literature [17].

## 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 Pre-Catalyst Synthesis

The pre-catalysts $[Fe(MeCN)_6][BF_4]_2$ **1**, $[Co(MeCN)_6][BF_4]_2$ **2** and $[Ni(MeCN)_6][BF_4]_2$ **3** were prepared as previously described [25]. A typical procedure for their preparation consists of mixing 12 mmol metal (purchased from Riedel) with 20 mmol $NOBF_4$ (purchased from Acros) in acetonitrile. The solution was stirred for 24 h. The unreacted metal was magnetically removed, 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 Synthesis

For the synthesis of the ionic liquid employed in this study, 1-butyl-3-methylimidazolium chloride (BMIC) was slowly added over $AlCl_3$, which had been sublimed once prior to use. The temperature was controlled in order to do not to exceed 30 °C. To complete the ionic liquid synthesis, the desired amount of co-catalyst, $AlEtCl_2$, $AlEt_2Cl$, $AlEt_3$ or MAO, was added, and the mixture was stirred overnight.

### 2.3 Catalytic Runs

The catalytic runs were performed using a Fisher-porter 200 mL, semi-continuous glass reactor equipped with a magnetic stirrer, a thermocouple, a continuous feed of ethylene at 10 bar, and 20 mL of 2,2,4-trimethylpentane. The pre catalyst was transferred to the reactor, followed by the addition of 20 mL of 2,2,4-trimethylpentane. After the system was purged with ethylene, 3 mL of the ionic liquid were added, starting the oligomerization reaction. The reaction was stirred for 0.5 h. The temperature was controlled by a thermostatic circulation bath. After the end of the reaction, the reactor was cooled to −60 °C and the organic phase was collected to immediate quantification of the products, without neutralizing the catalyst.

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: 36 °C for 15 min and heating rate of 5 °C/min until 250 °C. The productivity is expressed as turnover frequencies, TOF, defined as mol converted ethylene per mol pre-catalyst and by reaction time (in h).

## 3 Results and Discussion

The majority of oligomerization catalysts described in the current literature concerns nickel complexes. Their studies in ionic liquids are mostly concentrated in organoaluminate dialkylimidazolium ionic liquids, resulting in very high activity but also in high isomerization rates, giving mostly internally branched olefins. To understand this behavior, many aspects must be taken in account.

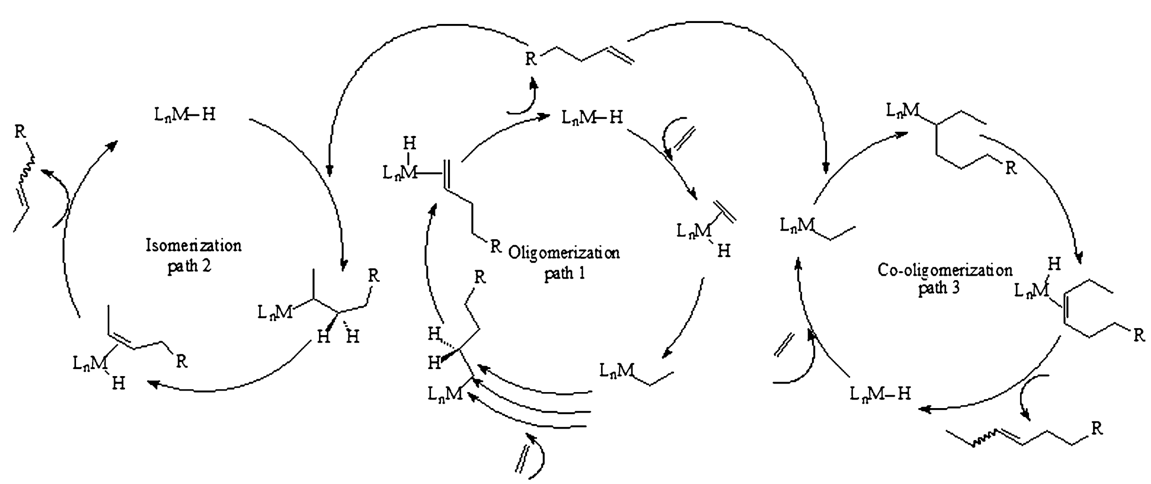
This behavior has been attributed to the fact that the active species in oligomerization can also catalyze side reactions, such as isomerization and co-oligomerization. Scheme 1 shows a general mechanism for oligomerization and side reactions. In this scheme, oxidation states and the different oligomers produced are not shown for the purpose of clarity.

The desired reaction is shown in path 1, which is responsible for the oligomerization of the primary products. The active species is regenerated after coordination of the olefin, chain growth, and termination by $\beta$-elimination, producing the primary oligomerization product. At this point, the active species could be used again in an oligomerization catalytic cycle, or it could isomerize the oligomerization product via path 2 and/or co-oligomerize these products through path 3.

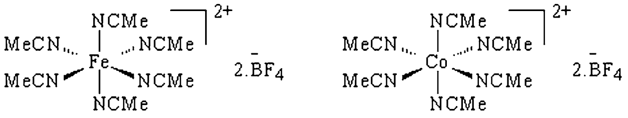
In the case of nickel-catalyzed oligomerization using dialkylimidazolium organoaluminate ionic liquids as the immobilization phase, the isomerization and co-oligomerization cycles becomes of considerable importance compared to the oligomerization cycle.

It is worth noting that many of these reactions are limited by mass transport [26]. This probably contributes to the low selectivity for $\alpha$-olefins for such oligomerization reactions. The amount of the active species that cannot follow path 1, due to the low availability of ethylene, follows path 2 or 3, consuming path 1 products. This mass control does not exclude the contribution of the nature of the catalysts themselves to the amount of substrate following the parallel path 2 and path 3 mechanisms.

Bis(imino)piridyl iron or cobalt has been successfully used as oligomerization catalysts [6], attracting great attention to iron and cobalt complexes for this reaction. The outstanding performance of such complexes makes



**Scheme 1** Mechanism for oligomerization of ethylene and possible side reactions



**Scheme 2** Structure of the pre-catalysts studied in this work [25]

them attractive subjects to be tested in ionic liquid biphasic catalysis conditions. For comparative studies, the cationic transition metal coordination compounds shown in Scheme 2 were chosen.

These coordination compounds were selected because the analogous nickel coordination compound is well known in the literature [17], and the analog was extensively described as being favorably used for comparison to the target cobalt and iron catalysts. These complexes have been evaluated in ethylene oligomerization, varying the reaction temperature and the nature of the associated co-catalyst, as shown in Table 1.

## 3.1 Ethylene Oligomerization with Iron

The iron compound, $[Fe(MeCN)_6][BF_4]_2$, **1**, is active under all conditions of oligomerization tested in this work. As shown in Table 1, entries 1–12, the oligomerization activity depends strongly on the nature of the co-catalyst as well as on the oligomerization temperature. Compared to the nickel analog, $[Ni(MeCN)_6][BF_4]$, **3**, the iron catalyst shows oligomerization activities *ca.* one order of magnitude lower than the nickel catalyst, as seen comparing entries 1–3 for iron with entry 24 for nickel with $AlEtCl_2$, or entries 4–6 for iron with entry 25 for nickel with $AlEt_2Cl$ as co-catalyst. As previously observed for nickel catalyst [27], more acidic co-catalysts, such as $AlEtCl_2$ and $AlEt_2Cl$ (entries 1 to 6), show higher activity than less acidic co-catalysts (entries 7 to 12), like $AlEt_3$ and MAO.

The iron/$AlEt_2Cl$ system (entries 4 to 6) and the iron/MAO system (entries 10 to 12) in chloroaluminate ionic liquid demonstrate an exponential dependency of activity with temperature. For these co-catalysts, no induction time was observed for the oligomerization, so the observed dependence of oligomerization activity with the temperature is due to the enhancement of the reaction rate with temperature. The calculation of apparent Arrhenius activation energies, plotting the logarithm of the turnover frequency with the reciprocal of the absolute temperature, gives values of 16 kcal/mol for the system iron/$AlEt_2Cl$ and 19 kcal/mol for the system iron/MAO. In the case of the nickel system, it was not possible to determine the activation energy due to the strong variation in the internal temperature in the reactor. The values observed for the iron and cobalt complexes can be compared with those available in the literature concerning nickel oligomerization or polymerization complexes, such as the values of 16.8 to 17.5 kcal $mol^{-1}$ reported by Ziegler and co-workers [28], or that of 16.3 kcal $mol^{-1}$ reported by Zhang and Lana [29].

The oligomerization reactions performed using $AlEtCl_2$ and $AlEt_3$ as co-catalysts show a different pattern for the dependence of activity with temperature. For the iron systems, the activity grows with an increase in the temperature from 10 °C to 30 °C (entries 1 and 2 for $AlEtCl_2$ as co-catalyst, entries 7 and 8 for $AlEt_3$), but decreases for further increases of the temperature to 50 °C (entries 2 to 3 for $AlEtCl_2$ and 8 to 9 for $AlEt_3$).

This behavior is often observed in the case of nickel complexes [30], and has generally been attributed to the formation of species with lower inherent activity or, more probably, to the partial decomposition or deactivation of the catalyst. A decrease in the ethylene concentration in solution at this oligomerization temperature, which would induce indirect catalyst decay, cannot be ruled out.

**Table 1** Biphasic oligomerization with iron, cobalt, and nickel catalysts dissolved in butyl-methyl-imidazolium organoaluminate ionic liquids

| Entry | Catalyst (μmol) | Temperature (°C) | Co-catalyst | [Al]/[M][d] | TOF ($h^{-1}$) | $C_4$ (wt%) | | $C_6$ (wt%) | $C_{\geq 8}$ (wt%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_4$ | 1-$C_4$ | | |
| 1 | **1**/21.5 | 10 | AlEtCl$_2$ | 120 | 1010 | 98.2 | 86.7 | 1.8 | – |
| 2 | **1**/18.5 | 30 | AlEtCl$_2$ | 140 | 16400 | 86.0 | 42.1 | 13.2 | 0.8 |
| 3 | **1**/20.4 | 50 | AlEtCl$_2$ | 120 | 12300 | 81.1 | 40.1 | 17.4 | 1.5 |
| 4 | **1**/19.9 | 10 | AlEt$_2$Cl | 130 | 560 | 98.7 | 91.2 | 1.3 | – |
| 5 | **1**/22.3 | 30 | AlEt$_2$Cl | 110 | 2800 | 95.8 | 78.4 | 4.2 | – |
| 6 | **1**/20.2 | 50 | AlEt$_2$Cl | 130 | 19500 | 79.0 | 27.5 | 19.0 | 2.0 |
| 7 | **1**/18.3 | 10 | AlEt$_3$ | 140 | 980 | 99.1 | 91.9 | 0.9 | – |
| 8 | **1**/16.0 | 30 | AlEt$_3$ | 160 | 14000 | 89.3 | 47.1 | 10.7 | – |
| 9 | **1**/15.1 | 50 | AlEt$_3$ | 170 | 8100 | 92.8 | 57.7 | 6.9 | 0.3 |
| 10 | **1**/16.6 | 10 | MAO | 160 | 70 | 100 | 100 | – | – |
| 11 | **1**/13.8 | 30 | MAO | 200 | 415 | 97.7 | 95.8 | 2.3 | – |
| 12 | **1**/18.1 | 50 | MAO | 150 | 4620 | 91.2 | 66.7 | 8.5 | 0.3 |
| 13 | **2**/16.5 | 10 | AlEtCl$_2$ | 150 | 230 | 97.9 | 96.8 | 2.1 | – |
| 14 | **2**/12.7 | 30 | AlEtCl$_2$ | 200 | 14100 | 87.4 | 48.8 | 12.5 | 0.1 |
| 15 | **2**/12.3 | 50 | AlEtCl$_2$ | 200 | 33200 | 66.7 | 21.0 | 30.0 | 3.4 |
| 16 | **2**/14.3 | 10 | AlEt$_2$Cl | 180 | 960 | 98.9 | 94.8 | 1.1 | – |
| 17 | **2**/18.2 | 30 | AlEt$_2$Cl | 140 | 4500 | 95.4 | 77.7 | 4.6 | – |
| 18 | **2**/16.9 | 50 | AlEt$_2$Cl | 150 | 19500 | 81.1 | 37.6 | 16.9 | 2.0 |
| 19 | **2**/16.3 | 10 | AlEt$_3$ | 160 | 140 | 97.3 | 98.7 | 2.7 | – |
| 20 | **2**/14.0 | 30 | AlEt$_3$ | 180 | 400 | 92.5 | 95.3 | 7.5 | – |
| 21 | **2**/18.4 | 50 | AlEt$_3$ | 140 | 350 | 91.1 | 95.8 | 8.9 | – |
| 22 | **2**/15.0 | 10 | MAO | 180 | 130 | 97.2 | 98.9 | 2.8 | – |
| 23 | **2**/13.8 | 50 | MAO | 200 | 668 | 98.0 | 96.0 | 2.0 | – |
| 24 | **3**/21.5 | 10[a] | AlEtCl$_2$ | 120 | 215000 | 42.6 | 14.5 | 36.2 | 21.5 |
| 25 | **3**/16.3 | 10[b] | AlEt$_2$Cl | 156 | 159000 | 68.1 | 18.4 | 26.6 | 5.3 |
| 26 | **1**/18.3 | 30[c] | AlEtCl$_2$ | 140 | 348 | 88.3 | 63.3 | 11.7 | – |
| 27 | **2**/12.7 | 30[c] | AlEtCl$_2$ | 200 | 88 | 76.5 | 87.0 | 23.5 | – |
| 28 | **4**/18.1 | 30 | AlEtCl$_2$ | 140 | 25900 | 73.3 | 27.9 | 24.2 | 2.5 |
| 29 | **5**/13.0 | 30 | AlEtCl$_2$ | 140 | 21800 | 76.1 | 29.3 | 21.4 | 2.5 |

Ionic liquid BMIC:AlCl$_3$:co-catalyst; molar ratio 1:1: 0.22; 30 min; 10 bar ethylene; **1** [Fe(MeCN)$_6$][BF$_4$]$_2$; **2** [Co(MeCN)$_6$][BF$_4$]$_2$; **3** [Ni(MeCN)$_6$][BF$_4$]$_2$ **4** FeCl$_2$; **5** CoCl$_2$

[a] Internal temperature increased to 85 °C

[b] Internal temperature increased to 65 °C

[c] Without ionic liquid

[d] Imprecision in [Al]/[M] ratio is ±30

The effect of the ionic liquid in the oligomerization reaction catalyzed by cationic iron complex can be seen comparing entries 2 with 26. It is remarkable the increase in activity of catalyst **1** upon addition of ionic liquid, from 348 $h^{-1}$ to 16400 $h^{-1}$. This enhancement shows the high ability of the ionic liquid to solvate the iron compound. A catalytic run performed with the organic phase obtained from the reaction of entry 2, after the separation from the ionic liquid, shows no further products formation, suggesting that the catalyst is quantitatively retained in the ionic liquid and the reaction occurs exclusively in the ionic liquid. The comparison of the catalytic behavior in entries 2 and 28 demonstrates that pre catalyst **4** is more active than **1**, but the absence of ligands results in considerably lower selectivity to α-olefins.

The iron catalyst shows high selectivity for ethylene dimerization, in the range 79.0% to 100%, with low amounts of trimers, C6 (0.9%, entry 7 to 19%, entry 6), and tetramers, C8 (maximum of 2.0% in entry 6). The high selectivity of the iron catalyst towards dimerization is attributed to the higher chain end rate ($\beta$-elimination reaction) as compared to the chain growth rate, an intrinsic characteristic of these catalytic species.

Otherwise, the selectivity towards trimers depends strongly on the temperature. For the system **1**/$AlEt_2Cl$, the amount of C6 grows from 2.0% at 10 °C to 19.0% at 50 °C. The growth in the selectivity towards hexenes can be attributed to the co-oligomerization of the primary products, butenes, with ethylene. Increasing the temperature increases both the formation of C4 and the formation of co-oligomerization products [31].

When $AlEt_3$ or MAO is used as a co-catalyst, the effects of the temperature are less pronounced than with the other co-catalysts studied in this work. Despite the low activity of the iron catalyst as compared to the nickel catalyst, the former resulted in systems more selective towards 1-butene than the latter.

### 3.2 Ethylene Oligomerization with Cobalt

The complex $[Co(MeCN)_6][BF_4]_2$, **2**, combined with $AlEtCl_2$ or $AlEt_2Cl$ shows better performance than association with $AlEt_3$ or MAO. The systems **2**/$AlEtCl_2$ or $AlEt_2Cl$ give TOF of 33000 and 19500 $h^{-1}$, entries 15 and 18 respectively, and TOF around 350 and 668 $h^{-1}$, entries 21 and 23 respectively, for $AlEt_3$ or MAO. Very similar behavior has been previously described for nickel complexes in homogeneous media [27].

It is worth noting the different effects of temperature on the activity of the different co-catalysts. The activity with the cobalt catalyst was very low at 10 °C for all co-catalysts, showing a TOF of less than 1000 $h^{-1}$. The increase of oligomerization temperature for the systems with $AlEtCl_2$ or $AlEt_2Cl$ as co-catalysts resulted in a substantial increase in activity. For $AlEt_3$ or MAO as co-catalysts, the effects of temperature on the activity are less pronounced. This clearly demonstrates the need for a stronger Lewis acid as co-catalyst for the activation of compound **2** for the oligomerization of ethylene.

The effect of the ionic liquid in the oligomerization reaction catalyzed by cationic cobalt catalyst can be seen comparing entries 14 with 27. As well as in the case of iron catalyst, an increase in activity of catalyst **2** occurs by addition of the ionic liquid, from 88 $h^{-1}$ to 14400 $h^{-1}$, demonstrating also the ability of these species to solvate the catalyst. Comparing the catalytic behavior in entries 14 and 29 demonstrates that pre catalyst **5** is more active than **2**, but the absence of ligands results in considerably lower selectivity to $\alpha$-olefins.

The cobalt and iron catalysts were very selective for the dimerization of ethylene. When $AlEtCl_2$ or $AlEt_2Cl$ were used as co-catalysts, the dimerization selectivity at different temperatures was very close to the system with iron, varying from 66.7% to 97.9% for $AlEtCl_2$ (entries 15 and 13), from 91.1% to 97.3% for $AlEt_3$ (entries 21 and 19) or even from 97.2% to 98.0% for MAO (entries 22, 23).

The selectivity for 1-butene with the cobalt catalyst is similar to that of the iron catalyst with respect to temperature. The tendency of higher isomerization with cobalt catalysts as compared to iron catalysts was also described in the homogeneous system [32].

## 4 Conclusion

Iron and cobalt catalysts have been shown to promote ethylene oligomerization in chloro-aluminate ionic liquids. The activity of these catalysts is lower than for analogous nickel catalysts, but they exhibit higher selectivity towards dimerization than the nickel analogs, enabling selective access to 1-butene. The highest activity for the iron system was 19,500 $h^{-1}$, while the highest activity for the cobalt system was 33,200 $h^{-1}$. In conditions of low activity, both systems showed high selectivity to 1-butene, higher than 86%. High activity generally corresponds to low selectivity, which shows the compromise between these concurrent tendencies. This suggests that the reaction suffers from mass transfer limitations. Olefins such hexenes or higher alkenes are mainly internal and branched. These olefins are mainly formed from co-oligomerization reactions, and their amounts are dependent on temperature.

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