

Nickel-catalyzed propylene dimerization in organochloroaluminate ionic liquids: Control of the isomerization reaction

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Abstract

Propylene dimerization has been studied in a biphasic system formed by $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ dissolved in 1-butyl-3-methylimidazolium organochloroaluminate ionic liquid (IL). The activity and dimerization selectivity show a high dependence on the reactional parameters and evidence of interfacial phenomena feature has been obtained. The isomerization of C_6 olefins could be minimized to 13% using a control of dimerization temperature and propylene pressure.

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1. Introduction

In the last years great attempts to achieve clean chemical processes have been developed. The use of ionic liquids (ILs) allows the recycle of the catalyst by a simple decantation of the catalyst solution from the products. A plethora of examples of the use of ILs in catalytic systems are nowadays available with promising results [1–5].

Among the most studied ILs are those of organochloroaluminate anions. The great interest in this type of IL, is the associative capacity of the aluminum species, which leads also to co-catalyst immobilization in the IL. This capacity led to this type of IL to be chosen for the Difasol process in Ref. [6], reducing catalyst and co-catalyst consumption when compared with the homogeneous system [7].

Several examples are described in the literature concerning the use of ILs in oligomerization reactions. Among these examples, we can note that the system is inactive when an organochloroaluminate IL with an aluminum molar fraction lower than 0.50 is employed [8]. It was also pointed out that ILs with an AlCl_3 molar fraction higher than 0.50 are not good solvents since they could promote the abstraction of ligands from

the catalyst [9,10]. This is the reason for the usual choice of neutral AlCl_3 -based ILs for oligomerization systems [11].

Despite the great potential of organochloroaluminate ILs for oligomerization reactions, there are no examples in the literature describing their use in oligomerization reactions for the synthesis of α -olefins. Examples of oligomerization reactions in organochloroaluminate ILs display a high degree of isomerization of the products in Ref. [12], and these ILs are considered to be responsible for the isomerization of the obtained olefins in Refs. [13,14], which is the major drawback in oligomerization reactions. In fact, there is only one example of a system, in which a high selectivity in α -olefins is achieved in Ref. [13], which was performed in a hexafluorophosphate ionic liquid. The control of the isomerization reaction is still a major goal in order to achieve the selective synthesis of terminal higher olefins.

The precatalyst $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ **1** is known to promote isomerization as a parallel reaction in oligomerization reactions in Ref. [15] constituting an appropriate subject for a careful study of the isomerization reaction in order to allow its control.

In the present work, the reaction parameters such as pressure, precatalyst amount $[\text{AlEtCl}_2]/[\text{Ni}]$ ratio (molar), stirring rate and temperature on propylene dimerization in organochloroaluminate IL are studied. The influence of these parameters in the isomerization and dimerization selectivity has been evaluated. Also we have assessed the influence on activity, and insertion modes of propylene with $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ **1** as

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precatalyst performed in a organochloroaluminate ionic liquid BMIC/ AlCl_3 / AlEtCl_2 with molar fraction 0.45/0.50/0.05 [16].

2. Experimental

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

2.1. Precatalyst preparation

The precatalyst $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$ has been prepared as previously described in Refs. [17,18], by mixing 12 mmol of metallic nickel (Riedel) to 20 mmol of NOBF_4 (Acros), in acetonitrile. The solution was kept under stirring for a day at 25°C . The unreacted nickel was removed with a magnetic bar and the solvent, was removed under reduced pressure. The complex was recrystallized from acetonitrile and, after decantation, excess solvent was removed and the complex dried under reduced pressure.

2.2. Ionic liquid synthesis

The ionic liquids were prepared by the slow addition of the requisite amount of 1-butyl-3-methylimidazolium chloride (BMIC) over previously sublimed AlCl_3 . The temperature was kept below 30°C and then the co-catalyst, AlEtCl_2 , was added. This ionic liquid was kept under stirring for 12 h.

2.3. Catalytic runs

The catalytic runs were performed in a double-walled steel reactor with a capacity of 120 mL, equipped with a magnetic stirrer, a thermocouple, with a continuous feed of propylene.

The precatalyst amount, ranging from 30 to $100\ \mu\text{mol}$, was added into the reactor under an argon atmosphere and followed by the addition of 35 mL of cyclohexane. The system was purged with propylene and the initial temperature of the reactor was

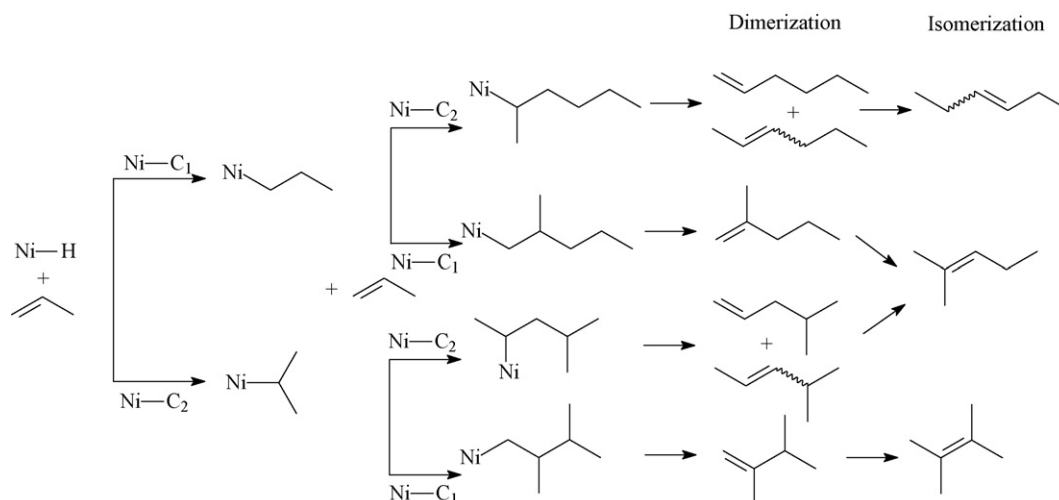
regulated at 15°C by a thermostatic circulation bath. By the addition of 3 mL of the ionic liquid BMIC/ AlCl_3 / AlEtCl_2 with a molar composition of 0.45/0.50/0.05, the reaction was started and the desired pressure was adjusted, ranging from 1 to 4 bar. The stirring rate was regulated ranging from 240 to 720 rpm, as indicated in each table. To study the influence of temperature on the system, the catalytic runs were performed in a double-walled glass reactor equipped with a magnetic stirrer and a thermocouple, with a continuous feed of propylene at 80 mbar and 7 mL of 2,2,4-trimethylpentane. The temperature ranged from -20 to 60°C .

After 30 min the reaction was stopped, the organic phase was withdrawal and immediately analyzed, without neutralization, by gas chromatography [19]. 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 $0.5\ \mu\text{m}$. Analysis conditions: 36°C for 30 min and a heating rate of $5^\circ\text{C}/\text{min}$ up to 250°C , maintaining 7 min at 250°C . The products were identified by co-injection method of standards and the use of *n*-decane as internal standard for quantification.

3. Results and discussion

The use of olefins with different fragments attached to the sp^2 carbons in dimerization reactions is a good tool for determining the mode of insertion of the olefin in the coordination sphere of the active species. This aspect is especially pertinent in the case of propylene dimerization, which allows a clear interpretation of the reactions that are happening since dimerization and isomerization products are easy to separate and identify. Scheme 1 shows the products of dimerization and isomerization of propylene.

Scheme 1 shows that the dimerization of propylene can be described by two successive insertions of the olefin in the catalytic species. Each insertion can occur through the C_1 or C_2 carbon of the propylene molecule, explaining the origin of the various hexene, methyl-pentene and dimethyl-butene isomers



Scheme 1. Mechanism for propylene dimerization.

produced. The mechanism above account for the regioselectivity for the insertion of propylene in the nickel species, which is classically evaluated using the parameters P and Q , defined in the literature in Ref. [20] as the selectivity for the formation of the nickel- C_1 species at the first and second insertion steps, as shown in Scheme 1. Eq. (1), where S_{1H} , S_{2H} , S_{3H} and S_{2M1P} represent the selectivity in 1-hexene, 2-hexenes, 3-hexenes and 2-methyl-1-pentene, respectively, enables the calculation of P and Eq. (2), where $S_{2,3DMB}$ represents the selectivity in 2,3-dimethylbutenes, enables the calculation of Q .

$$P = \sum S_{1H} + S_{2H} + S_{3H} + S_{2M1P} \quad (1)$$

$$Q = \sum S_{2M1P} + S_{2,3DMB} \quad (2)$$

In addition to P and Q , the effect of the experimental parameters on the propylene oligomerization is evaluated in terms of dimerization selectivity (S_{C_6}) and in terms of isomerization selectivity (S_I). As shown in Scheme 1 the isomerization capacity of the system is expressed as the sum of the selectivity in 3-hexenes, 2-methyl-2-pentene, and 2,3-dimethyl-2-butene present in the dimer fraction, since they uniquely originate from the isomerization of dimerization products.

The catalytic activity is expressed as turn over frequency (TOF, mol of converted propylene per mol of precatalyst per hour).

3.1. Effect of the propylene pressure

Table 1 shows the effect of the pressure on the catalytic behavior of **1** as precatalyst in propylene dimerization using BMIC/ $AlCl_3$ / $AlEtCl_2$ IL with a composition 0.45/0.50/0.05.

It can be observed that the increase in propylene pressure, from 1 to 4 bar, Entries 1–4, leads to a slight decrease in isomerization. This behavior has already been observed in the dimerization of ethylene-catalyzed by **1** in IL in Ref. [12]. As nickel-hydride species can be active both in oligomerization and isomerization, the effect of the propylene pressure can be explained as a result of the competition between the insertion of a new propylene molecule in the Ni–H bond and the coordination of a previously formed dimer.

The increase of the turnover frequency from 8.5 to $29.9 \times 10^3 \text{ h}^{-1}$, upon increasing the pressure from 1 to 4 bar, Entries 1–4, respectively, was accompanied with an increase of the temperature ranging from 30 °C at 1 atm to 70 °C at

Table 1
Effect of the pressure on propylene dimerization with the system $[Ni(MeCN)_6][BF_4]_2$ /BMIC/ $AlCl_3$ / $AlEtCl_2$

Entry	Pressure (bar)	S_{C_6} (%)	S_I (%)	P (%)	Q (%)	TOF (10^3 h^{-1})
1	1	80	59	27	14	8.5
2	2	81	56	28	14	21.8
3	3	80	55	28	14	25.2
4	4	80	53	28	14	29.9

General conditions: 100 μmol precatalyst amount; stirring rate 600 rpm; $[AlEtCl_2]/[Ni] = 30$.

4 bar, underestimating the true effect of pressure on isomerization.

The most pronounced increase of activity with pressure was observed at low pressures, from 1 to 2 bar. When the pressure increased from 3 to 4 bar, the increase of the activity was less pronounced. Similar behavior, albeit more pronounced, has been described by Svedja and Brookhart in the homogeneous dimerization of propylene in Ref. [21] catalyzed by a cationic α -diimine-nickel (II) catalyst. With this system, at high propylene pressures, the activity is independent of the pressure. The authors proposed the formation of an equilibrium between two kinds of catalytic species: an alkyl agostic nickel species, predominant at reduced pressures and an alkyl olefin nickel species, predominant at higher pressures. The increase of pressure shifts the equilibrium in the direction of the alkyl olefin nickel species. When the alkyl olefin nickel complex becomes the unique species present, this corresponds to the complete displacement of the equilibrium, and the activity becomes independent of the pressure.

The activity of **1** in ILs increases slightly with the pressure as can be seen in Entries 2–4. This behavior can be explained by the low solubility of the olefins in ILs in Ref. [22], which does not allow the complete displacement of the above-mentioned equilibrium, differently of the behavior in usual organic solvents.

3.2. Effect of stirring

Table 2 shows the results of the variation of stirring on propylene dimerization with **1**/BMIC/ $AlCl_3$ / $AlEtCl_2$ performed in an IL with a composition 0.45/0.50/0.05. It can be seen that an increase in stirring affects the dimerization selectivity (S_{C_6}), isomerization (S_I) and activity (TOF) in propylene dimerization, but has only a slight effect on the selectivity as indicated by the values of P and Q , which are virtually unaffected.

The increase of activity values with the increase of stirring is a clear indication that the reaction is mainly interfacial, i.e., it is under diffusional control. These results are not surprising due the extremely high activity showed by this catalyst.

The most pronounced effect of the variation of the stirring rate is observed in the amount of isomerization (S_I). When the system is stirred at 240 rpm, 33% of C_6 products are isomerized, Entry 5, and when the stirring rate is increased the C_6 isomerization value rises and attains 59% for a 600 rpm stirring, Entry 8. Such an effect can be attributed to an increase of the

Table 2
Effect of the stirring on propylene dimerization with the system $[Ni(MeCN)_6][BF_4]_2$ /BMIC/ $AlCl_3$ / $AlEtCl_2$

Entry	Stirring (rpm)	S_{C_6} (%)	S_I (%)	P (%)	Q (%)	TOF (10^3 h^{-1})
5	240	86	33	25	10	0.6
6	360	84	38	26	11	2.4
7	480	80	46	26	11	3.8
8	600	80	59	27	14	8.5
9	720	79	56	27	13	8.6

General conditions: 100 μmol precatalyst amount; pressure 1 bar; $[AlEtCl_2]/[Ni] = 30$; temperature 25 ± 5 °C.

Table 3

Effect of the precatalyst amount and $[\text{AlEtCl}_2]/[\text{Ni}]$ on propylene dimerization with the system $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2/\text{BMIC}/\text{AlCl}_3/\text{AlEtCl}_2$

Entry	1 (μmol)	$\text{AlEtCl}_2/\text{Ni}$	S_{C_6} (%)	S_1 (%)	P (%)	Q (%)	TOF (10^3h^{-1})
10	30	95	86	51	27	12	29.1
11	37	78	84	52	26	12	26.5
12	67	43	83	57	26	13	18.8
13	96	30	80	59	27	14	8.5
14*	100	95	78	58	22	15	11.3

General conditions: pressure 1 bar; stirring rate 600 rpm; temperature $30 \pm 5^\circ\text{C}$; *BMIC/AlCl₃/AlEtCl₂ 0.34/0.50/0.16.

contact surface between the catalyst and olefin phases' interface, with the stirring, demonstrating that the isomerization reaction is mainly interfacial.

3.3. Effect of the precatalyst amount and $[\text{AlEtCl}_2]/[\text{Ni}]$ ratio

The results of the influence of the precatalyst amount and $[\text{AlEtCl}_2]/\text{Ni}$ ratio on propylene dimerization performed with **1**/BMIC/AlCl₃/AlEtCl₂ system are shown in Table 3.

Comparing Entries 10–13, an increase in activity can be observed with a decrease of the amount of precatalyst. It is pertinent to note that an increase in activity with lower amounts of transition metal complex is often observed in oligomerization systems, and is usually ascribed to the fact that low amounts of the precatalyst are effectively transformed to active species and the excess of inactive material does not give rise to an increase in products and the turnover frequency decreases.

Furthermore, it is pertinent to recall that the $[\text{AlEtCl}_2]/[\text{Ni}]$ ratio decreases when the amount of nickel increases. This is because all other parameters are maintained constant, including the amount of aluminum species. The direct dependence of the activity with the $[\text{AlEtCl}_2]/[\text{Ni}]$ ratio was observed with the same precatalyst in homogeneous media in Ref. [23], but in this case it is not so pronounced, probably because the majority of the aluminum is incorporated in the structure of the IL.

With respect to the insertion modes of propylene, no meaningful changes are observed in Table 3. Analyzing the effect of the amount of precatalyst on the selectivity, a low decrease in dimerization selectivity occurs with an increase of amount of precatalyst, concomitant with an increase in isomerization. This is explained in terms of the low availability of propylene leading to a co-dimerization reaction and increase in isomerization.

3.4. Effect of the temperature

The most remarkable effect of the reaction parameter on the system **1** as a precatalyst in propylene dimerization using BMIC/AlCl₃/AlEtCl₂, is the influence of the reaction temperature. Table 4 shows the results of runs performed between -20 and 60°C .

From Table 4, it is clear that the isomerization decreases significantly at low temperatures. This signifies that the initial products of dimerization are 1- and 2-hexene, 4-methyl-2-pentene, 4-methyl-1-pentene, 2-methyl-1-pentene and

Table 4

Effect of the temperature on propylene dimerization with the system $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2/\text{BMIC}/\text{AlCl}_3/\text{AlEtCl}_2$

Entry	Temperature ($^\circ\text{C}$)	S_{C_6} (%)	S_1 (%)	P (%)	Q (%)	TOF (10^3h^{-1})
15	-20	97	13	25	7	1.5
16	0	89	32	25	10	3.4
17	10	82	45	25	12	5.7
18	30	72	59	25	15	8.9
19	60	68	63	27	18	4.9

General conditions: $32 \pm 2 \mu\text{mol}$ precatalyst amount; stirring rate 600 rpm; $[\text{AlEtCl}_2]/[\text{Ni}] = 30$; pressure 80 mbar.

2,3-dimethyl-1-butene and that these products isomerizes, giving all other observed products. The large dependence of isomerization on temperature suggests that this side reaction occurs due to the low steric hindrance of the catalyst since in systems with bulky ligands isomerization levels are lower [24].

With respect to dimerization selectivity, the results of Table 4 strongly suggest that heavier oligomers, obtained at higher temperatures, originate from the co-dimerization reaction of hexenes with the incoming propylene.

It is worth noting that the selectivity in the first step (P) is constant, at approximately 25% of insertions through the C_1 carbon of the incoming propylene, but the second insertion varies, starting with 7% of insertions through the C_1 carbon at -20°C and increasing to 18% at 60°C . This signifies that the original trend is the insertion through the C_2 carbon, as expected from the most stable intermediate, but with an increase in temperature there is an increase in the motion of the fragments and consequently a tendency to enhance the amount of C_1 insertions since this generates a less crowded intermediate.

4. Conclusion

An appropriate control of reactional parameters is necessary in order to achieve a maximal selectivity in dimerization and minimal isomerization. Furthermore, activity was highly dependent on these parameters. The insertion modes of propylene were not affected under the conditions employed, except in the case of a change in temperature. The solubility of propylene in the IL plays an important role in the dimerization of propylene which is characteristic of an interfacial reaction. It has been demonstrated that the isomerization observed in propylene is due to the nature of the catalyst. Finally, it was demonstrated that a suitable choice of conditions in propylene dimerization allows the control of

isomerization, an undesirable side reaction in oligomerization systems.

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