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Biphasic oligomerization of ethylene with nickel–1,2-diiminophosphorane complexes immobilized in 1-*n*-butyl-3-methylimidazolium organochloroaluminate

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Abstract

Nickel(II)–diiminophosphorane complexes combined with alkylaluminum co-catalysts are active for the oligomerization of ethylene under biphasic reaction conditions. As observed in homogeneous phase, the selectivity (dimers vs higher oligomers) is related to the nature of the diiminophosphorane ligands. In 1-*n*-butyl-3-methylimidazolium organoaluminate ionic liquids, an enhancement of the catalytic activity and convergence of the selectivity are observed upon repeating cycles. These data suggest that organoaluminate anions replace the diiminophosphorane ligands in the coordination sphere of the active nickel species.

Keywords: Biphasic oligomerization; Nickel iminophosphoranes; Organoaluminate ionic liquids

1. Introduction

The problem of separating solvents and catalysts from reaction products is a major issue in homogeneous catalysis. Biphasic technologies can overcome this difficulty and ionic liquids, which are not miscible with organic derivatives, have recently emerged as versatile catalyst solvents [1,2].

The oligomerization of olefins is a prominent example among biphasic technologies in which the oligomers and the organoaluminate ionic liquid form immiscible layers. After the desired reaction time, the upper phase can be withdrawn, and the catalyst is quantitatively retained in the reactor as a solution in the ionic liquid. A fresh olefin is fed, initiating the second cycle of the reaction, and this procedure is repeated successively for long residence runs.

Intriguing dependencies of the catalyst behavior on the nature of the anions that constitute the ionic liquids have been observed [3,4]. These feature raised the question of whether ionic liquids act only as solvents or can participate more directly in the catalytic process. Herein, we present experimental evidence of catalyst modifications *via* ligand exchange involving classical ionic liquids.

Olefin oligomerization is a major industrial process [5] and nickel complexes are the most frequently employed catalysts [6]. High-performance Ni catalysts that selectively produce oligomers have been obtained by tailoring the surrounding ligands [5]. We have shown that diiminophosphorane Ni(II) complexes **1–4** (Scheme 1), combined with alkylaluminum co-catalysts, are highly active for the ethylene oligomerization in homogeneous phase [7].

Of particular interest is the fact that the oligomer distribution varies in a wide range depending on the ligand carbon backbone nature. These characteristics make these systems good candidates for the study of the fate of Ni active species in ionic liquids.

2. Experimental

The reactions were performed under argon using standard Schlenk tube techniques. Solids were dried under reduced

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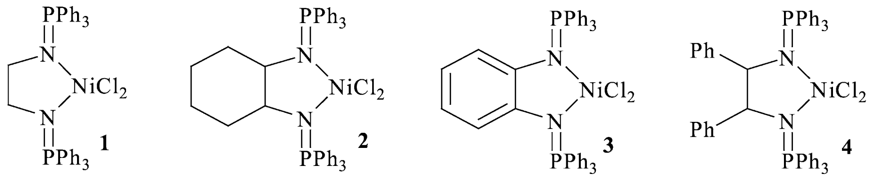


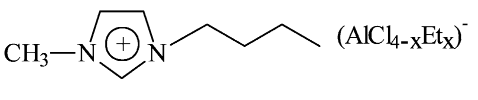
Scheme 1.

pressure and chlorobenzene was distilled over 3 Å molecular sieves, immediately prior to use. Diethylaluminum chloride ($AlEt_2Cl$) was purchased from Aldrich and was used as received. Complexes **1**–**4** have been synthesized as previously described [7].

Ethylene oligomerization reactions were performed in a 120-ml double-walled glass reactor equipped with magnetic stirring and a thermocouple, with continuous feed of ethylene at 1.1 bar. The reaction temperature was controlled by a thermostatic circulation bath. A typical reaction run was performed by introducing 90 µmol of the nickel (II) complex in 20 ml of cyclohexane. The system was saturated with ethylene, and then 3 ml of 1-*n*-butyl-3-methylimidazolium organochloroaluminate (Scheme 2), synthesized as previously described [8] and represented as MBI-Al, were added for the biphasic runs, or a solution of $AlEt_2Cl$ for the homogeneous runs (Al/Ni molar ratio of 70). The ethylene pressure is maintained at the desired value and continuously fed. After 2 h, the stirring was stopped and the phases were allowed to separate. The upper organic layer was removed by means of a cannula. The second cycle started by repressurization of the reactor. The organic phase was weighed and analyzed by gas chromatography. This chromatographic analysis was performed on a Varian 3400CX equipment, with a Petrocol HD capillary column (methyl silicone, 100 m long, i.d. 0.25 mm, and film thickness 0.5 µm) working at 36 °C for 15 min and then heating to 250 °C at a rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$.

3. Results and discussion

Organoaluminate-based ionic liquids were selected for this study because (i) we are using a Ziegler–Natta type catalytic system and (ii) biphasic technologies using nickel catalysts working in organoaluminate dialkylimidazolium ionic liquids have proved to be extremely attractive from both the economic and industrial points of view [9]. The ionic liquid was formed by mixing equimolar quantities of dialkylimidazolium chloride and $AlCl_3$ followed by addition of $AlEt_2Cl$ co-catalysts, achieving an Al molar fraction of 0.57 [8]. In order to establish reliable comparisons between the experiments conducted under homogeneous (chlorobenzene) and biphasic conditions, the catalytic systems were examined at a temperature of 10 °C, under an ethylene pressure of 1.1 bar and a reaction time of 2 h (Table 1).



Scheme 2.

Nickel(II)-diiminophosphorane complexes **1**–**4** are highly active for ethylene oligomerization under mild reaction conditions both in homogeneous and biphasic conditions (Table 1). The results observed in chlorobenzene (entries 1, 5, 8, 12) follow the previously established general trends, although the reaction conditions are quite different [7]. A dramatic evolution of the catalytic activity and oligomer distribution was observed upon repeating catalytic runs in ionic liquids (Table 1). With all the pre-catalysts **1**–**4**, a regular increase of the catalytic activity, estimated by the turnover frequency (TOF), was recorded (Fig. 1). The TOF's after three cycles are nearly three times as high as the first cycle values.

Different factors, such as modification of the polarity of the medium [10] or of the aluminum counteranions [11], can contribute to this rate enhancement. However, this evolution can also be due to displacement of the diiminophosphorane ligands leading to new highly active catalytic species. This last hypothesis is supported by comparison of the distribution of dimers (mainly internal butenes) and higher oligomers upon repeated cycles. As observed in homogeneous phase, the selectivity in C_4 varies in a wide range (30–49%) according to the nature of the diiminophosphorane ligands (Fig. 2). In contrast, after three cycles all the C_4 selectivities converged to the same value of 25 ± 1% (Table 1, Fig. 2). The selectivities in higher oligomers (C_{6-12}, Table 1) also regularly increased upon repeating cycles and

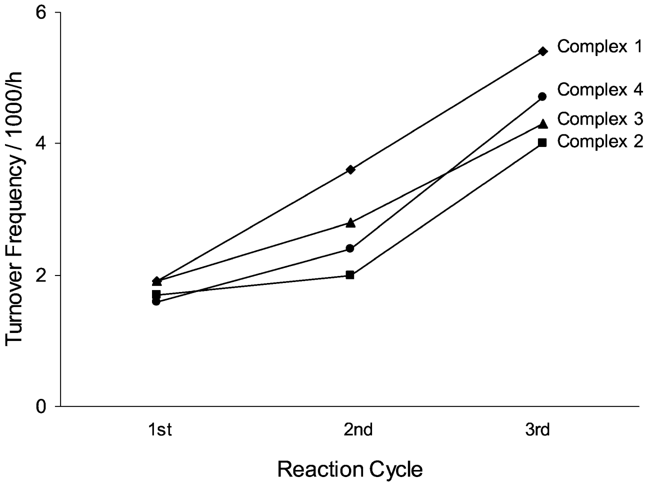


Fig. 1. Evolution of the turnover frequency of complexes **1**–**4** in MBI.Al upon repeating cycles.

Table 1
Ethylene oligomerization with complexes **1**–**4** under homogeneous and biphasic conditions

Entry	Solvent	Complex	Cycle[a]	Yield	TOF[b]	C_4		C_{6-12}
				(g)	$\times 10^{-3}$ (h^{-1})	Total/%	α^c/%	Total/%
1	PhCl	**1**	—	25	4.7	36	2	64
2	MBI-Al	**1**	1st	9.4	1.9	31	7	69
3	MBI-Al	**1**	2nd	18	3.6	24	7	76
4	MBI-Al	**1**	3rd	28	5.4	25	7	75
5	PhCl	**2**	—	15	3.0	58	1	42
6	MBI-Al	**2**	1st	8.5	1.7	40	7	50
7	MBI-Al	**2**	3rd	20	4.0	24	6	76
8	PhCl	**3**	—	16	3.2	51	1	49
9	MBI-Al	**3**	1st	9.6	1.9	30	8	70
10	MBI-Al	**3**	2nd	14	2.8	29	7	71
11	MBI-Al	**3**	3rd	22	4.3	26	1	74
12	PhCl	**4**	—	9.2	1.8	64	6	36
13	MBI-Al	**4**	1st	8	1.6	49	6	51
14	MBI-Al	**4**	2nd	12	2.4	32	5	67
14	MBI-Al	**4**	3rd	24	4.7	25	5	74

Reaction conditions: magnetically stirred 120 ml double-walled glass reactor, constant ethylene pressure at 1.1 bar, 90 µmol of nickel complex, 20 ml of cyclohexane, 10 °C, 2 h, 3 ml of 1-*n*-butyl-3-methylimidazolium organochloroaluminate.

[a] Biphasic runs: 1st cycle performed with 20 ml of cyclohexane, 2nd and 3rd cycles performed without addition of solvents.

[b] TOF = turnover frequency: mol of ethylene converted by mol of Ni-complex and by hour.

[c] α = alpha olefin content in the C_4 fraction, i.e., 1-butene.

are higher than those obtained in the homogeneous phase (Table 1).

These data strongly suggest that the diiminophosphorane ligands are slowly displaced from the Ni-coordination sphere by other ligands, leading to a unique type of active species. It is clear that in the ionic liquid most coordinating species are chloroaluminate anions, of general formula $(AlCl_{4-x}Et_x)^-$ [12], arising from the equilibrium between $AlCl_4^-$ and $AlEt_2Cl$. Furthermore, complexes in which a Ni center is linked to chlorine atoms of aluminate species are known [13]. Thus, we propose that the α-diiminophosphorane ligands are progressively displaced by the organoaluminate species, giving rise to more active but less selective Ni-systems containing organoaluminate anions as ligands.

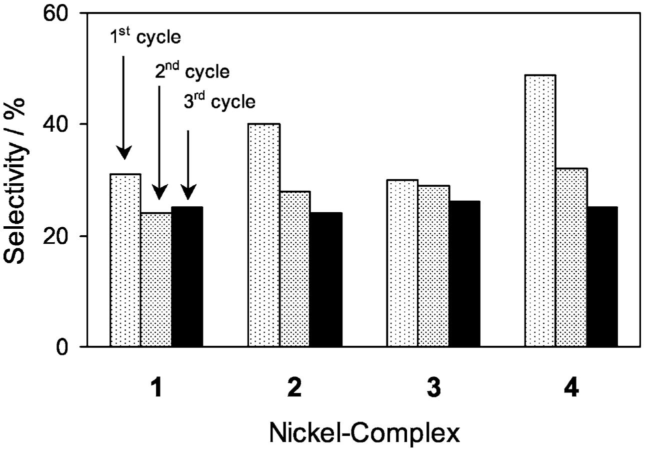


Fig. 2. Evolution of the selectivity in C_4 upon repeating cycles in MBI-Al biphasic oligomerization of ethylene with Ni complexes **1**–**4**.

Our results show that these chloroaluminates counterions can displace tightly bound chelates such as diiminophosphoranes. In conclusion, organoaluminate ionic liquids are not suitable solvents for Ziegler–Natta type Ni catalysts modified by classical neutral organic ligands.

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References

[1] (a) P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3773;
(b) T. Welton, Chem. Rev. 99 (1999) 2071.
[2] (a) S. Einloft, F.K. Dietrich, R.F. de Souza, J. Dupont, Polyhedron 15 (1996) 3257;
(b) Y. Chauvin, H. Olivier-Bourbigou, Chemtech 25 (1995) 26.
[3] D. Sémeril, H. Olivier-Bourbigou, C. Bruneau, P.H. Dixneuf, Chem. Commun. (2002) 146.
[4] J. Dupont, R.F. de Souza, P.A.Z. Ziani, Chem. Rev. 102 (2002) 3667.
[5] (a) J. Skupinska, Chem. Rev. 91 (1991) 613;
(b) W. Keim, Angew. Chem. Int. Ed. Engl. 29 (1990) 235;
(c) W. Keim, A. Behr, B. Limbacker, C. Krüger, Angew. Chem. Int. Ed. Engl. 22 (1983) 503;
(d) Y. Chauvin, H. Olivier, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, Wiley–VCH, New York, 1996, p. 245;
(e) B. Bogdanovic, B. Spliethoff, G. Wilke, Angew. Chem. Int. Ed. Engl. 19 (1980) 622.

[6] W. Keim, Angew. Chem. Int. Ed. Engl. 29 (1990) 235.
[7] M. Sauthier, F. Leca, R.F. de Souza, K. Bernardo-Gusmão, L.F.T. Queiroz, L. Toupet, R. Réau, New J. Chem. 26 (2002) 630.
[8] Y. Chauvin, H. Olivier, C.N. Wyrvalski, L.C. Simon, R.F. de Souza, J. Catal. 165 (1997) 275.
[9] Recently IFP announced the disponibility of the new Difasol technology for the dimerization of olefins: M. Freemantle, Chem. Eng. News 76 (1998) 32.
[10] J. Dupont, P.A.Z. Suarez, R.F. de Souza, R.A. Burrow, J.-P. Kintzinger, Chem. Eur. J. 6 (2000) 2377.
[11] (a) T.J. Melton, J. Joyce, J.T. Maloy, J.A. Boon, J.S. Wilkes, J. Electrochem. Soc. 137 (1990) 3865;
(b) R.J. Gale, B. Gilbert, R.A. Osteryoung, Inorg. Chem. 17 (1978) 2728;
C.L. Hussey, in: G. Mamantov, C. Mamantov (Eds.), Advances in Molten Salts Chemistry, Vol. 5, Elsevier, New York, 1983, p. 185;
(c) S. Tait, R.A. Osteryoung, Inorg. Chem. 23 (1984) 4352;
(d) A.A. Fannin Jr., D.A. Floreani, L.A. King, J.S. Landers, B.J. Piersma, D.J. Stech, R.L. Vaughn, J.S. Wilkes, J.L. Williams, J. Phys. Chem. 88 (1984) 2614;
(e) J. Fuller, R.T. Carlin, H.C. De Long, D. Haworth, J. Chem. Soc. Chem. Commun. (1994) 299.
[12] In fact the anionic species existing in organoaluminate ionic liquids have been identified as complex anions with the formulation $[\mathrm{AlCl}_{4-x}\mathrm{Et}_x + b(\mathrm{AlCl}_3)]^-$, where $b = 0$, 1, or 2 (for details on the identification of such species see Ref. [11]).
[13] B. Bogdanovic, Angew. Chem. Int. Ed. Engl. 12 (1973) 954.