Iron(II)–ethylene polymerization catalysts bearing 2,6-bis(imino)pyrazine ligands
Part II. Catalytic behaviour, homogeneous and heterogeneous insights

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Abstract

A series of new iron(II) complexes bearing tridentate pyrazine-bis(2,6-arylimino) ligands where the aryl groups are 1-naphthyl, 2,6-dimethylphenyl, and 2,6-diisopropylphenyl have been used as ethylene polymerization catalysts after activation with alkylaluminiums. The new complexes display a lesser catalytic activity than those bearing the corresponding pyridine-bis(2,6-arylimino) ligands. Varying the steric bulkiness of the aromatic groups in the tridentate ligands and the polymerization conditions affects the catalytic productivity.
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1. Introduction

Dramatic advances in metallocene catalyst technology beginning in the early 1980s have affected the polyolefins industry and resulted in a number of new commercial processes for the preparation of polyolefinic materials with new or improved performance parameters [1]. In order to extend the range of polyolefinic materials produced, considerable effort has been devoted to the discovery of new families of catalysts during the last decade. Of particular interest are those catalysts that allow either for greater control over the polymer properties of established polyolefinic materials or for the production of new materials.

For a long time, most attention has been focused on early transition metal systems, even if some earlier work on nickel catalyst systems of the type employed in the shell higher olefin process (SHOP) had revealed the potential for late transition metal to polymerize olefins. An important advance in late transition metal polymerization catalyst technology was described by Brookhart and co-workers, who showed that Ni(II) and Pd(II) complexes incorporating bulky α-diimine ligands (Fig. 1) are capable of polymerizing ethylene and α-olefins to high molar mass polymers [2–5]. Late transition metals are particularly attractive because of their lesser oxophilicity, resulting in a greater tolerance for heteroatom-containing functionalities. This fact opens up the possibility for copolymerizations of polar monomers. The protective bulk of the *ortho*-substituents above and below the metal centre proved to be critical to the molecular weight of the resulting polyethylene [11].

In 1998, in parallel studies, Gibson and coworkers [6,7] and Brookhart and coworkers [8,9] groups have independently described iron and cobalt based extremely active catalysts for the polymerization of ethylene when activated with methylaluminoxane (MAO). These 2,6-bis(imino)pyridine type catalysts (Fig. 2) allowed the polymerization chemistry to enter the "iron age" as described by Wass and Gibson [10]. The two great advantages of these systems over existing homogeneous catalysts are their low cost and the ease with which chemists can derivatise the complexes. Here again, the catalyst structure is the key to the activity.

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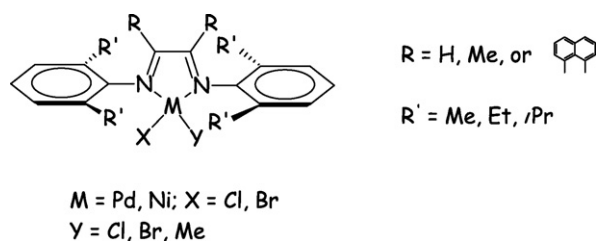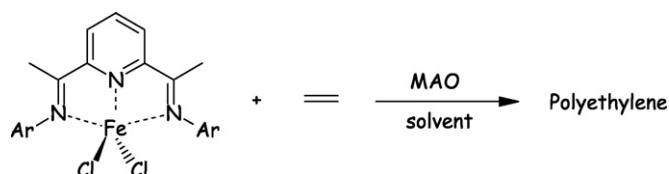*E-mail address:* AF.Noels@ulg.ac.be (A.F. Noels).

Fig. 1. α-diimine-based metal complexes for ethene polymerization.

Fig. 2. bis(imino)pyridine-based metal complexes for ethene polymerization.

We report here that altering the electronic density distribution on the catalyst precursor by replacing the central pyridinyl ring of the ligand by a pyrazinyl one (an heterocycle of similar steric bulk but of different electronic properties) considerably modify the catalyst efficacy. We also describe the effects brought about by varying different reaction parameters such as hydrogen pressure, the presence of a comonomer, the temperature of polymerization, and the polymerization activity with silica supported catalysts.

2. Results and discussion

2.1. Homogeneous polymerization

The catalytic efficiency of iron bis(imino)pyrazine complex (PYZ), bearing 2,6-dimethylimino "side arms" was tested in ethylene polymerization using MMAO as the cocatalyst and compared to that of its bis(imino)pyridine analogue (DIP), see Fig. 3.

The polymerization reactions were carried out in a parallel autoclave bench with eight independent reactors called "Endeavor" and provided by the Argonaut technologies. For the present project, reaction temperatures ranging from either 30 or 50 °C and pressure of 10 bar of ethylene were generally used. The temperature, pressure and ethylene consumption inside the reactors were continuously monitored by the tailor-made software control. To reach and maintain inert conditions

inside the reactors, the reactors were evacuated through a condenser line while being heated at 120 °C prior to the injection of any sensitive component. Liquid sample were injected via syringe through septa-capped injection ports which could be closed by valves. MMAO was chosen as the co-catalyst with an aluminium:metal ratio of 1500. A small amount of TIBAL was used as poison scavenger for conditioning of the reactors and was injected together with the solvent under a nitrogen atmosphere. The MMAO was used for activation and solubilization of the metal complexes. The activated solutions were injected into the reactors into an ethylene atmosphere. After a reaction time of 1 h, excess monomer was vented from the reactors and the polymerization reaction quenched by addition of ethanol.

The reactions were thus performed at different temperatures with a 10 bar pressure of ethylene. Upon treatment with MMAO, complex PYZ and its pyridinyl analogue DIP give active ethylene polymerization catalysts. These catalyst systems do not show any induction period, an immediate ethylene consumption being generally observed.

The following subsections detail and quantify the data resulting from precatalyst modifications together with the effect of various experimental conditions on ethylene polymerization. Table 1 shows the results of polymerization performed at five different temperatures (30, 40, 50, 60 and 70 °C) at an ethylene pressure of 10 bar.

The iron complex based on the substituted pyridine ligand (DIP) appears as a much more active ethylene polymerization catalyst than the corresponding complex based on the pyrazine ligand (PYZ). The molecular weights of the polymers formed are also quite different. Whereas the well known 2,6-bis(imino)pyridyl iron complex provides higher molecular weight polyethylenes (M_W around 2×10^5), the PYZ-based catalyst yield only low M_W polyethylene. The second observation that can be made is that the productivity of the bis(imino)pyrazine catalyst (PYZ) slightly increases with the temperature whereas an opposite effect is observed in the case of the bis(imino)pyridine-based catalyst (DIP) for which the efficiency decreases with the temperature. These results are in good agreement with those reported by Britovsek et al. [14] for iron 2,6-bis(imino)pyridyl ligands. Thus, the introduction of a second nitrogen atom on the aromatic ring of the ligand has a clear-cut influence on the polymerization activity.

The presence of a hydrogen pressure in the polymerization reactor can also influence both the yield and the molecular weight distribution of the polymer formed, which was also borne
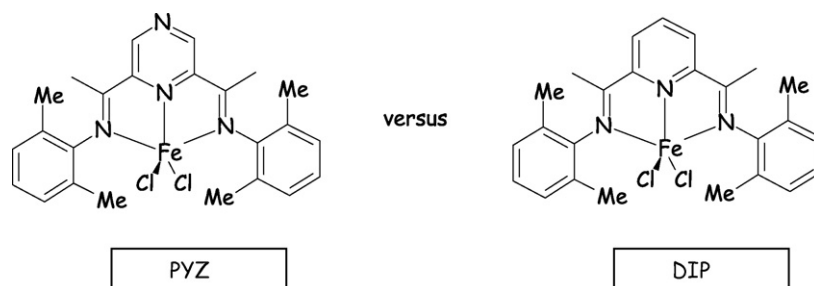

Fig. 3. Structurally similar Pyrazine-based (PYZ) and Pyridine-based (DIP) Fe precatalysts for ethene polymerization.

Table 1
Polymerization results

| Ligand	Precatalyst (µmol)	Al/metal (mol/mol)	T (°C)	$P_{ethylene}$ (bar)	Yield (g)	Activity (g_{PE}/mmol h)	M_W (Da)
PYZ	0.4	1500	30	10	0.061	153	22000
PYZ	0.4	1500	40	10	0.061	153.3	n.d.
PYZ	0.4	1500	50	10	0.063	156	12000
PYZ	0.4	1500	60	10	0.065	161.8	n.d.
PYZ	0.4	1500	70	10	0.062	154	n.d.
DIP	0.0075	1500	30	10	0.618	82427	260630
DIP	0.0075	1500	40	10	0.627	83533	225427
DIP	0.0075	1500	50	10	0.539	71907	127574
DIP	0.0075	1500	60	10	0.471	62840	214849
DIP	0.0075	1500	70	10	0.213	28347	16630
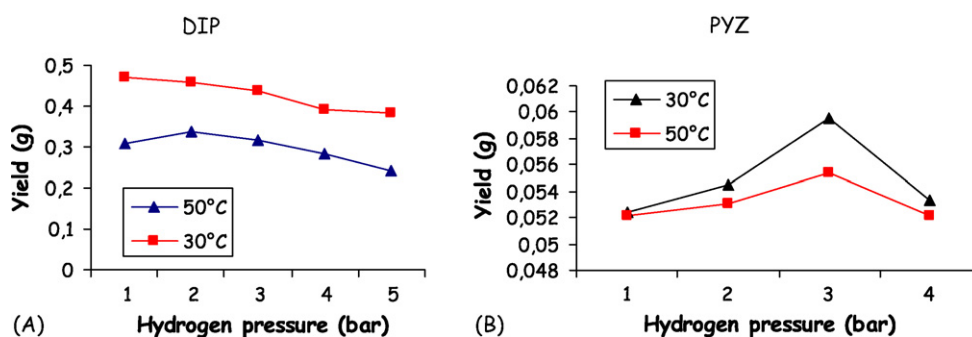
Fig. 4. Influence of hydrogen pressure on the polymer yield with complexes DIP and PYZ, respectively.

out by the facts in the present study. The effects of a hydrogen pressure are reported in Fig. 4. The data (Fig. 4A) confirms the tendency already observed with DIP: the polymer productivity decreases as the temperature rises. In addition, a hydrogen pressure further decreases the DIP activity (from 0.6 g of polymer at 30 °C without hydrogen to 0.47 g in its presence) and the polymerization activity decreases slightly with hydrogen pressure. The same observation is made at 50 °C with this catalyst precursor.

PYZ behaves differently from DIP (Fig. 4B), the polymerization activity increases with hydrogen pressure up to a pressure of 3 bar, at 30 °C as at 50 °C. Above this pressure value, the activity falls down dramatically, though in this case, the ethylene polymerization is favoured at lower temperatures. So, hydrogen presence in the reaction medium favours the polymerization reaction with PYZ catalyst, 3 bar being the optimal hydrogen pressure.

A few experiments of ethylene polymerization in the presence of hexene as a comonomer were also carried out and the results are summarized in Table 2. In the case of the PYZ complex, the presence of hexene does not have a strong influence (if any) on the polymerization activity of the catalyst, at 30 °C as well as at 50 °C. However, a different behavior is observed with DIP for which the presence of hexene in the reaction medium depresses the polymerization activity to some extent after activation by MMAO. The polymerization activity falls off as the amount of hexene injected in the reactor increases.

From the comparisons between PYZ and DIP precatalysts under various experimental conditions, it appears that these two metal complexes behave in significantly different manners after activation by MMAO, the metallic complex bearing the pyridine ligand moiety being much more active towards ethylene polymerization than the one bearing the pyrazine moiety.

2.2. Heterogeneous polymerization

To date, the use of the [bis(imino)pyridyl] iron(II) complexes in a continuous process has been difficult, as the polyolefins produced will deposit at the reactors walls and the stirring device, a problem which might be overcome by tailoring the polymer morphology via heterogenization of the homogeneous compounds.

The silica supported iron naphthylbis(imino)pyrazine complex can be readily obtained by mixing the MAO-modified silica with the iron complex in toluene. The naphthyl (**3**) and diisopropyl (**2**) bis(imino)pyrazine silica supported iron(II) catalysts (Fig. 5) were used in the ethylene polymerization experiments. The slurry polymerization was performed under standard conditions in an autoclave; at 80 °C, with 10 bar ethylene pressure

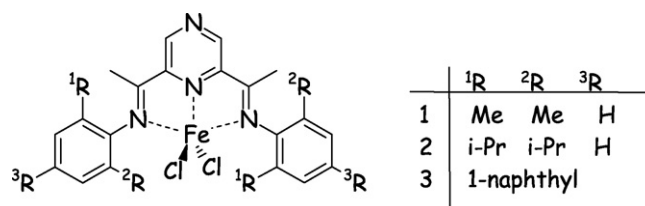|	¹R	²R	³R
1	Me	Me	H
2	i-Pr	i-Pr	H
3	1-naphthyl		

Fig. 5.

Table 2
Ethylene polymerization in the presence of a co-monomer

Ligand	Precatalyst (μmol)	Al/metal (mol/mol)	T (°C)	Time (min)	P_{C2} (bar)	Hexene (ml)	Yield (g)	Activity (g_{PE}/mmol h)
PYZ	0.4	1500	30	60	10	0	0.061	153
PYZ	0.4	1500	30	60	10	0.25	0.0494	123.5
PYZ	0.4	1500	30	60	10	0.5	0.0584	146
PYZ	0.4	1500	30	60	10	0.75	0.0588	147
PYZ	0.4	1500	30	60	10	1	0.0584	146
PYZ	0.4	1500	50	60	10	0	0.063	156
PYZ	0.4	1500	50	60	10	0.25	0.0571	142
PYZ	0.4	1500	50	60	10	0.5	0.0529	132
PYZ	0.4	1500	50	60	10	0.75	0.0563	140
PYZ	0.4	1500	50	60	10	1	0.0547	136
DIP	0.0075	1500	30	60	10	0	0.331	44133
DIP	0.0075	1500	30	60	10	0.25	0.384	51227
DIP	0.0075	1500	30	60	10	0.5	0.502	66933
DIP	0.0075	1500	30	60	10	0.75	0.345	45947
DIP	0.0075	1500	30	60	10	1	0.015	1960
DIP	0.0075	1500	50	60	10	0	0.709	95547
DIP	0.0075	1500	50	60	10	0.25	0.426	56733
DIP	0.0075	1500	50	60	10	0.5	0.463	61707
DIP	0.0075	1500	50	60	10	0.75	0.404	53840
DIP	0.0075	1500	50	60	10	1	0.38	50613

and using either triisobutylaluminium (TIBAL) or tetraisobutyl-dialuminoxane (TIBAO) as the cocatalyst. The polymerization results are summarized in Table 3. Entries 1–3 concern catalyst precursor (**3**), whereas entries 4 and 5 are related to catalyst precursor (**2**).

The polymerization activity of the silica supported naphthyl- and isopropylbis(imino)pyrazine iron complexes is modest and in line with the trend usually observed with heterogenized catalysts, that is lower than that of an equivalent amount of homogeneous catalyst.

Table 3
Heterogeneous polymerization results

	Run				
	1	2	3	4	5
Catalyst	**3**	**3**	**3**	**2**	**2**
Catalyst amount (mg)	300	300	300	300	300
Co-catalyst	TIBAL	TIBAO	TIBAO	TIBAO	TIBAL
Amount (ml)	4.5	3	3	3	4.5
Al (mmol)	1.5	1.5	1.5	1.5	1.5
Temperature (°C)	80	80	50	80	80
Solvent (*n*-hexane) (l)					
Amount	2	2	2	2	2
Ethylene pressure (bar)	10	10	10	10	10
H_2 pressure (bar)	1	1	1	1	1
Time (min)	120	120	120	120	120
Yield (g)	4.3	8.6	3	2.4	2.1
Activity (g_{PE}/g_{cat} h)	7	14	5	4	4
Productivity (g_{PE}/g_{cat})	4	29	10	8	7
Analyses					
M_n (Da)	826	825	825	883	824
M_W (Da)	884	885	883	897	881
M_W/M_n	1.07	1.07	1.07	1.02	1.07

The two catalyst systems yield low M_W polymers (DP ≈ 30) but of surprisingly narrow polydispersities. The productivity of catalyst (**3**) goes up by using TIBAO instead of TIBAL as the cocatalyst. The yield of the reaction increases about two-fold when the catalyst precursor is activated by tetraisobutyldialuminoxane. This observation is not borne out when catalyst precursor bears isopropyl groups. Indeed in the case of catalyst precursor (**2**), changing the activator nature does not significantly modify the polymerization activity. Furthermore, decreasing the reaction temperature has not a beneficial effect on the issue of the reaction (compare entries 2 and 3). Nevertheless, using TIBAO as the cocatalyst at the temperature of 50 °C, provides results similar in terms of catalyst activity and productivity to those obtained at 80 °C with TIBAL as the cocatalyst. The two iron-complexes tested in these experiments are thus rather poor heterogeneous ethylene polymerization catalyst precursors although they yield polymer of very narrow polydispersity. The complex bearing the 2,6-diisopropyl moiety is less active than the one bearing the naphthyl moiety. This fact demonstrates once again that the structure of the catalyst precursors is a key parameter that influences greatly the outcome of polymerizations.

3. Conclusion

Bisiminopyrazine complexes of iron form active ethylene polymerization catalysts both in the homogeneous and heterogeneous phase when activated by aluminium alkyls. However, they display a much lesser activity than their pyridine analogues. The introduction of a second nitrogen atom at the *para* position of the pyridinyl ring of the ligand backbone decreases significantly not only the polymerization activity of the resulting catalytic species but also the molecular weight of the polymers formed,

the latter displaying a very narrow polydispersity when activated by TIBAL or TIBAO cocatalysts. The reasons for the different behaviors are not clear. Coordination of the aluminium cocatalyst to the "*para*" nitrogen atom of the pyrazine ring might interfere with the coordinating ability of the tridentate ligand and/or modify the geometry of the active complex (counter anion also possibly involved). The unexpected formation of polymers having low M_W is indicative that β-hydrogen elimination takes place and is greatly favored when compared to the apparently "similar" pyridine-based analogues.

4. Experimental

All manipulations were carried out under an atmosphere of argon using standard Schlenk and cannula techniques. Argon was purified by passage through columns of BASF R3-11 catalysts and 4 Å molecular sieves. Solvents were refluxed over an appropriate drying agent and distilled under argon prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer FTIR 1720×. Melting points (m.p.) were determined with an electrothermal apparatus without further correction. Anilines were used directly as purchased without further purification.

4.1. MAO-modified silica support preparation

The MAO deposition on the silica carrier was carried out in a Büchi 1 dm^3 glass autoclave, equipped with a Julabo FP40 temperature controlling unit. Mechanical stirring was applied at the stirring speed of 200 rpm. Silica carrier (30.8 g of Grace Sylopol® 948, dried for 16 h at 600 °C) and toluene (200 ml) as solvent were introduced in the nitrogen purged reactor. A 52.5 ml of a MAO (14.65 g MAO; SiO_2/MAO = 100/47.5) solution in toluene (Crompton Eurecen® 5100/30T methylalumoxane = 30 wt.%, density = 0.93) were added drop-wise via a pressure-equilibrated dropping funnel. At the end of the addition, the suspension was heated at reflux under stirring for 3 h. After cooling at room temperature, silica was transferred in a glass filter funnel (frit porosity: G3) with a glass stopcock on the sidearm and a Rotaflo stopcock on the lower outlet. Silica has been washed with toluene (3× 150 ml), finally rinsed with hexane (3× 150 ml) and dried under dynamic vacuum at room temperature for 4 h.

4.2. Synthesis of the silica-MAO supported catalyst based on MePyzNaphtFeCl$_2$

In a conditioned 100 ml three-neck flask, 5–6 g of silice-MAO were transferred and the exact weight was determined by weight difference. Then 50 ml of toluene (or enough to suspend the solid) and the iron specie (59.7 mg) were introduced in the flask and stirred mechanically during 2 h. The solid is finally filtered under nitrogen, rinsed with toluene and then with hexane. The final product is then well dried under vacuum.

4.3. General procedure for ethylene polymerization

4.3.1. Catalyst sample preparation

In a schlenk, conditioned under nitrogen, the appropriate amount of toluene (~22.5 ml, in fact enough to reach 25 ml after addition of the co-catalyst) is added. Iron complexes are weighted under air in 1.5 ml vials (stored in a dessicator). Depending of the catalyst activity potential, 1–3 mg of active species is weighted. Under agitation, the vial containing the active species is dropped in the toluene in order to dissolve it. Up to know all complexes were completely soluble at such concentration. The appropriate amount of the co-catalyst solution is added as precontact almost 10 min before catalyst injection.

4.3.2. Endeavor conditioning and polymerization

Eight glass vessels and eight peek impellers, previously conditioned in an oven at 70 °C for at least 1 h, were inserted in the endeavor assembly which was then duly sealed and conditioned by several cycles of pressurizing with dry nitrogen and venting at 80 °C.

Then the reactors assembly was cooled down to room temperature and the required amount of hexane was introduced via the ball valves with a syringe equipped with stainless steel needle.

Thus, following the temperature program set in the endeavor controlling unit, each of the reactors was brought to the set-point temperature and pressure of ethylene and/or hydrogen.

Then the desired aliquot of catalyst solution prepared as described above was manually injected into each of the reactors vessels via the corresponding ball valve using a glass syringe equipped with a stainless steel needle. The introduction of the catalyst started the polymerization reaction. Ethylene pressure was kept at setpoint by continuous introduction of ethylene by the automated control of the endeavor device.

At the end of the required polymerization time, the catalyst was quenched by the addition of ethanol and the reactor vessels were cooled to room temperature and vented. The major amount of solvent (hexane) is evaporated simply in the hood for the night and the polymer is then dried in a oven (70 °C, under vacuum) for at least 1 h to remove the residual solvent (toluene). Each reaction vessels is weighted to estimate productivity.

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