

Supported Hybrid Catalysts based on Zirconocene and Tris(pyrazolyl)borate Titanium Derivatives

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ABSTRACT: A series of hybrid supported catalysts were prepared by combining (*i*BuCp)₂ZrCl₂ and {Tp^{M^s*}}TiCl₃ complex (Tp^{M^s*} = HB(3-mesityl-pyrazolyl)₂(5-mesityl-pyrazolyl)⁻) sequentially grafted onto MAO (methylaluminoxane)-modified silica according to a Plackett-Burmann 2³ design. Supported catalysts were prepared taking into account the immobilization order, silica pretreatment temperature, and grafting temperature. Grafted metal content was comparatively determined by Rutherford backscattering spectrometry (RBS), X-ray photoelectronic spectroscopy (XPS), and inductively coupled plasma-optical emission spectroscopy (ICP-OES). The resulting catalysts were evaluated in terms of catalyst activity and polymer properties. According to RBS measurements, grafted metal content remained comprised between 0.1 and 0.5 wt % Zr/SiO₂ and

0.1 and 0.3 wt % Ti/SiO₂ depending on the immobilization order and on silica pretreatment temperature. All the systems were shown to be active in ethylene polymerization having external MAO as cocatalyst. Catalyst activity seemed to be governed by the zirconocene species, influenced slightly by Ti ones. Resulting polymers were characterized by DSC and GPC. The polyethylenes mostly presented higher molecular weight than those produced by homogeneous catalysts or by zirconocene grafted on bare or on MAO-modified silica. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2002–2009, 2006

Key words: supported metallocene; tris(pyrazolyl)borate titanium; hybrid catalysts; ethylene polymerization; silica

INTRODUCTION

The polyolefin market is still growing and new grades of polyolefins with particular properties are demanded for several application in different fields. The development of new catalysts is one of the most important key factors for determining and controlling the polyolefin's properties. The discovery of metallocene catalysts represented an important milestone in the polymerization catalysts not only by their high activity, but also due to their high selectivity for the synthesis of well-defined polyolefins. However, homogeneous catalysts possess some disadvantages in industrial application, since most of the Ziegler-Natta plants run with heterogeneous catalysts. The immobilization of such catalysts on supports, especially on silica-based materials, allows to overcome such inconveniences, although this approach is usually accompanied by a reduction in catalysts activity due to generation of some inactive species and to the steric

effect played by the support surface, which acts as a huge ligand.¹

New generations of nonmetallocene catalysts have been proposed in the literature.² The aim is to develop new systems (the so-called postmetallocene catalysts), which, besides not being covered by patents, are capable to afford further improvements in polymer product properties and production flexibility. Because of such advances, current market prospects for metallocenes and other single-site catalysts appear to be booming with long-term growth rate projections. While metallocene catalysts are very versatile, the new nonmetallocene single-site catalysts provide several advantages, among them their chemical synthesis being much more straightforward in many cases than that of the metallocene.

Among the postmetallocene catalysts, one can cite those based on group 4 metals,^{3–6} especially those using Ti as metal center with a wide variety of ligands including tris(pyrazolyl)borate.^{7–12} Tris(pyrazolyl)borate ligands have been widely used in coordination and organometallic chemistry as stabilizing groups in high-oxidation state transition metal complexes because of their strong electron donor ability.^{13–15} Recently, we have studied the chemistry of group 4 complexes, bearing sterically hindered tris(pyrazolyl)-

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borate ligands, aiming at designing novel olefin polymerization catalysts. Our studies demonstrated that the presence of mesityl substituents at the 3(5)-position of pyrazolyl rings establishes the formation of highly active catalyst species for ethylene polymerization.^{16–20} For instance, the $\{\text{Tp}^{\text{Ms}^*}\}\text{TiCl}_3$ complex ($\text{Tp}^{\text{Ms}^*} = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$) exhibits activities as high as 9.0×10^3 kg of PE/mol Ti h·atm with the production of essentially linear polyethylene having molecular weight distribution (MWD) between 4 and 15, depending of the polymerization conditions.¹⁶

In polymer processing, the molecular weight (M_w) and MWD are important factors, since they determine both the mechanical and the rheological properties, respectively. Metallocenes are characterized by producing polymers with narrow molecular weight and composition distributions, which may lead to many improvements in physical properties, such as clarity, impact, and environmental crack resistance. On the other hand, polyethylenes with a broad MWD show greater flowability in the molten state at high shear rate, which is important for blowing and extrusion techniques.

Several methods for controlling the M_w and MWD of polymers have been proposed. From the technological point of view, one approach is to carry out the polymerization in a series of reactors, presenting different polymerization conditions such as temperature, pressure, and hydrogen partial pressure. However, this method involves additional processes and increases in capital costs. A second possibility is to blend the polymers produced by individual catalysts. Although blending can control M_w and the MWD of polymers, miscibility problems can take place. Finally, another approach involves the combination of two or more transition metal catalysts bearing different responses to hydrogen and monomer in a single reactor, thus producing polymers with different M_w ranges.¹⁹ López-Linares, studying catalyst combinations between a commercial Ziegler-Natta catalyst and other catalysts, observed that the MWD is slightly affected by the nature of metallocenes and tris(pyrazolyl)borate titanium derivatives.²¹

Thus, commercialization of metallocene technology can be partially hampered by two factors: the necessity of developing supported metallocene catalysts and of producing polymers with broader MWD. The use of two different metallocene compounds was already proposed to produce bimodal polyethylene (PE), which processability was improved.²² Polymer properties were also controlled by using mixtures of metallocene compounds, considering the known individual responses to polymerization process variables as the basis for polymer design.²³

Concerning supported systems, most of the studies consist in the development of hybrid catalysts combin-

ing Ziegler-Natta and metallocene catalysts.^{24,25} A few reports involving the immobilization of two metallocene on the same support are reported in the literature. MWD and chemical composition of copolymer were shown to be controllable by the combination of metallocenes such as $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{Cp}_2\text{HfCl}_2$ and $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{CGCTi}$ (CGC = constrained geometry catalysts).²⁶ $\text{Me}_2\text{C}(\text{Cp})-(2,7\text{-}(t\text{-Bu})_2\text{FluZrCl}_2$ and $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$,²⁷ $\text{Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrCl}_2$ and $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ ²⁸ were also co-supported on silica-based materials.

In previous studies, we produced hybrid catalysts by grafting CpTiCl_3 on a fourth generation Ziegler-Natta catalyst,²⁹ by supporting $(n\text{BuCp})_2\text{ZrCl}_2$ and Cp_2NbCl_2 ³⁰ or Cp_2ZrCl_2 and $(n\text{BuCp})_2\text{ZrCl}_2$ ³¹ on silica-based materials under different experimental conditions. In the present study, a zirconocene and non-metallocene catalyst, namely $(i\text{-BuCp})_2\text{ZrCl}_2$ and $\{\text{Tp}^{\text{Ms}^*}\}\text{TiCl}_3$ ($\text{Tp}^{\text{Ms}^*} = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$) were grafted on MAO-modified silica support according to a Plackett Burmann 2³ design. The resulting grafted metal content in the supported catalysts was determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES), Rutherford backscattering spectrometry (RBS), and X-ray photoelectronic spectroscopy (XPS). Hybrid-supported catalysts were tested in ethylene homopolymerization, having MAO as cocatalyst. Polymers were characterized by their molecular weight, crystallinity, polydispersity, and melting (T_m) temperature.

EXPERIMENTAL

Materials (chemicals)

Silica Grace 948 ($255 \text{ m}^2 \text{ g}^{-1}$) was activated under vacuum ($P < 10^{-4} \text{ m bar}$) for 16 h at 723 K. The support was then cooled to room temperature under dynamic vacuum and stored under dried argon. MAO (Witco, 10.0 wt % toluene solution, average molar mass 900 g mol^{-1}) and $(i\text{-BuCp})_2\text{ZrCl}_2$ (Witco) were used without further purification. Ethylene, provided by COPESUL Co., and argon were deoxygenated and dried through columns of BTS (gently supplied by BASF) and activated molecular sieve (13 Å) prior to use. Pure-grade toluene were deoxygenated and dried by standard techniques before use. The synthesis of $\{\text{Tp}^{\text{Ms}^*}\}\text{TiCl}_3$ ($\text{Tp}^{\text{Ms}^*} = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$) is described elsewhere.¹⁶

Preparation of supported catalysts

The supported catalysts were prepared according to a 2³ factorial design for multivariate analysis,³² and the studied variables were as follows: impregnation temperature (303 or 353 K), activation temperature of the silica (373 or 723 K), and sequence of addition of the

TABLE I
2³ Factorial Design Employed in the System Confection

Essay	Factor			Response			
	Cat1	T_{sup} (K)	T_{graft} (K)	wt % Zr/SiO ₂		wt % Ti/SiO ₂	
				RBS	ICP	RBS	ICP
1	Ti	373	303	0.4	0.3	0.2	0.1
2	Ti	373	353	0.2	0.1	0.2	0.1
3	Ti	723	303	0.2	0.2	0.1	0.1
4	Ti	723	353	0.1	0.1	0.3	0.1
5	Zr	373	303	0.5	0.5	0.1	0.1
6	Zr	373	353	0.5	0.3	0.1	0.2
7	Zr	723	303	0.4	0.2	0.1	0.1
8	Zr	723	353	0.3	0.2	0.2	0.3

catalyst (Zr or Ti-based catalyst). Analysis of variance at the 95% confidence level was employed to evaluate the calculated effects.

All grafting experiments were performed under inert atmosphere using the Schlenk technique. Chemically modified silicas were prepared by impregnating 1.0 g of activated silica Grace 948 with a toluene MAO solution, corresponding to 4 wt % Al/SiO₂, at room temperature for 1 h. The solvent was removed by vacuum, and then, solutions of the catalyst (*i*-Bu)₂ZrCl₂ and {Tp^{M_s*}}TiCl₃ corresponding to 0.25 wt % M/SiO₂ (for each catalyst) was added and stirred for 1 h at 298 or 353 K depending on the essay (see Table I). The slurry was then filtered through a fritted disk. The resulting solids were washed with 15 × 2.0 cm³ of toluene and dried under vacuum for 4 h.

Catalyst characterization

Inductively coupled plasma–optical emission spectroscopy

The metal contents (Ti and Zr) were measured by ICP–OES. The samples were previously attacked by acid digestion using H₂SO₄ 2*N* solution.

Rutherford backscattering spectrometry

Zr and Ti loadings in catalysts were determined by RBS using α -particle beams of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. The method is based on the determination of the number and the energy of the detected particles that are elastically scattered in the Coulombic field of the atomic nuclei in the target. In this study, the M/Si atomic ratio was determined from the heights of the signals corresponding to each of the elements in the spectra and converted to wt % M/SiO₂. For an introduction to the method and applications of this technique, the reader is referred elsewhere.^{33,34}

X-ray photoelectron spectroscopy

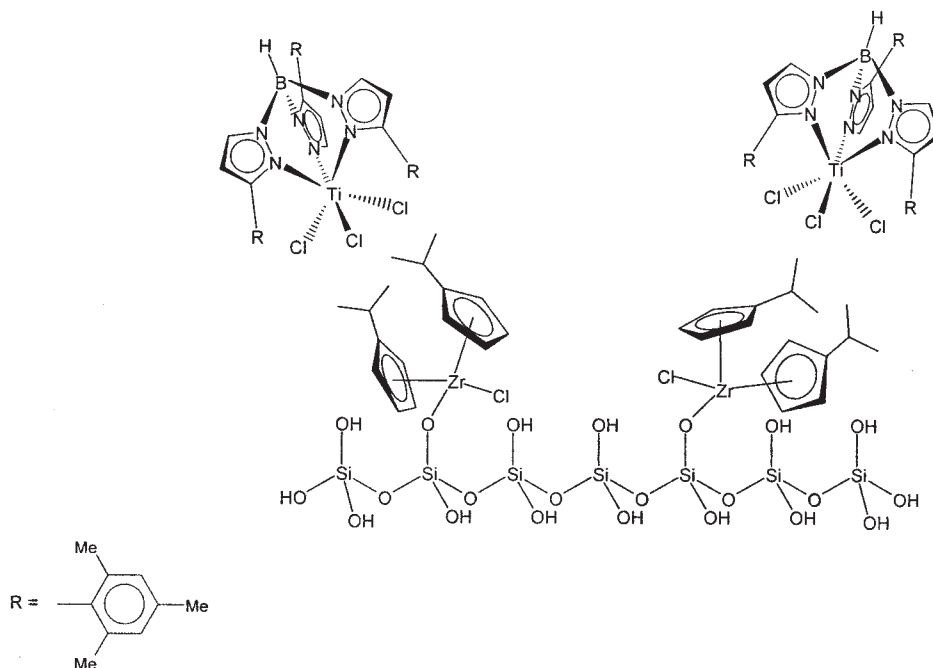
The X-ray photoelectron spectra (XPS) were obtained on a PHI 5600 Esca System (Φ Physical Electronics), using monochromated Al K α radiation (1486.6 eV). Spectra were taken at room temperature in low-resolution (pass energy 235 eV) in the range of 1000–0 eV and in high-resolution (pass energy 23.5 eV) modes for the Si (2p), Al (2p), Zr (3d^{5/2}), Ti (2p), and Cl (2p) regions.

The samples were mounted on an adhesive copper tape as thin films. Samples were prepared in a glove box, transferred under nitrogen atmosphere, and then, evacuated at 10⁻⁶ Torr by a turbomolecular pump in an introduction chamber for 90 min. During data collection, the ion-pumped mass chamber was maintained at 5 × 10⁻⁹ Torr. Each sample was analyzed at a 75° angle relative to the electron detector. Normally, 50 scans were signal averaged for selected binding energy windows and processed by the software supplied by the manufacturer. Neutralizer environment was 21.5 mA.

Binding energies examined (element, transition, approximate binding energy, and range scanned) were as follows: Si 2p, 103.3 eV, 96–108; Al 2p, 72.9 eV, 70–80; Zr 3d^{5/2}, 178.9 eV, 176–188 eV; Ti 2p, 460 eV, 455–469 eV; and Cl, 2p, 200 eV, 195–207 eV. All binding energies values were charge-referenced to the silica Si 2p at 103.3 eV.

Estimation of surface atomic ratios involved integrated areas and calculated atomic sensitivities factors, which were empirically derived for the electron energy analyzer supplied by Perkin–Elmer: (Si (2p)), 56.65; (Al (2p)), 57.59, (Zr (3d^{5/2})), 439.98; Ti (2p), 12.741; and Cl (2p), 5.161.

Three measurements per sample were made, and the reproducibility of the XPS analysis was confirmed. For each of the XPS spectra reported, an attempt has been made to deconvolute the experimental curve in a series of peaks that represent the contribution of the photoelectron emission from atoms in different chem-



Scheme 1 Grafted surface species.

ical environments. These peaks are described as a mixture of Gaussian and Lorentzian contributions to take into account the effects of the instrumental error on the peak-shape characteristic of the photoemission process.

Polymerization reactions

Ethylene homopolymerizations were performed in 0.25 dm³ of toluene in a 1.00-dm³ Pyrex glass reactor connected to a constant temperature circulator and equipped with mechanical stirring and inlets for argon and the monomer. MAO was used as cocatalyst in an Al/M (Zr + Ti) = 2000. For each experiment, a mass of catalyst system corresponding to 10⁻⁶ mol L⁻¹ of M was suspended in 0.01 dm³ of toluene and transferred into the reactor under argon. The polymerizations were performed at atmospheric pressure of ethylene at 333 K for 30 min. Acidified (HCl) ethanol was used to quench the processes, and reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at 333 K. Each polymerization reaction was repeated at least three times under identical conditions, leading to similar products.

Polyethylene characterization

Polymer melting points (T_m) and crystallinities were determined on a DuPont DSC 2910 differential scanning calorimeter calibrated with Indium, using a heating rate of 10 K min⁻¹ in the temperature range 313–

513 K. The heating cycle was performed twice, but only the results of the second scan are reported, because the former is influenced by the mechanical and thermal history of the samples. For gel permeation chromatography (GPC) analysis, 2 mg of polyethylene was dissolved in 4 mL of 1,2,4-trichlorobenzene (TCB) in the oven at 453 K for 1 h. Molar masses and molar mass distributions were investigated with a Waters GPCV 2000 high-temperature GPC instrument, equipped with viscometrical detector and four columns (107, 107, 106E, and 140). TCB was used as solvent at a flow rate of 1 mL min⁻¹. The analyses were performed at 413 K. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low-density polyethylenes and polypropylenes.

RESULTS AND DISCUSSION

Silica is one of the simplest oxides, because its surface, at least for moderate temperatures of activation, is mainly composed of isolated, and to a lesser extent, vicinal and geminal hydroxyl groups, as well as relatively unreactive siloxane bridges. Lewis acid/base sites are absent, unless it has been activated at very high temperatures, and Brønsted acidity is low or nonexistent.³⁵ The number of silanol groups on a fully hydroxylated silica surface has been found to be about 4.9 OH nm², regardless of the type of silica.³⁶ Thermal treatment reduces this number to about 1.2–1.5 OH nm² by silanol condensation for silicas activated at 723 K.³⁷ The OH silanol groups are capable to react with

TABLE II
Principal Effect of Each Variable and Interaction Between Effects On Metal Content

Effect	Zr/SiO ₂ (wt %)		Ti/SiO ₂ (wt %)	
	RBS	ICP	RBS	ICP
T_{graft}	-0.1300	0.0025	0.1375	0.0450
T_{sup}	-0.1750	2.2375	-0.0125	-0.0100
CatI	0.2500	-1.0975	-0.0075	-0.0050
(T_{graft} and T_{sup})	0.0500	1.8325	-0.0025	0.0200
(T_{graft} and CatI)	0.0150	-1.7925	0.0425	0.0150
(T_{sup} and CatI)	-0.0500	1.1725	-0.0175	0.0000
(T_{graft} and T_{sup} and CatI)	0.0250	1.9725	-0.0325	0.0150

hydrogen-sequestering agents, such as organometallic chlorides and alkoxides. Thus, the immobilization of the organometallic compound takes place by elimination of one or more of the original ligands.

In the previous study, we evaluated the effect of silica thermal treatment and grafting temperature³⁸ of MAO content in silica modification³⁹ and of the steric effect impinged by ligands in metallocene catalysts⁴⁰ on the catalyst grafted content, on catalyst activity, and on polymer properties. On the basis of these previous results, we decided to perform a study of the influence of silica pretreatment temperature of grafting and of the order of catalyst addition in grafting (*i*BuCp)₂ZrCl₂ and {Tp^{M_s*}}TiCl₃ sequentially on a MAO-modified silica support. It is worth mentioning that according to previous study, higher catalyst activity was found in the case of grafting (*n*BuCp)₂ZrCl₂ on MAO-modified silica bearing 2–4 wt % Al/SiO₂.⁴¹ Similar results were observed in the case of grafting {Tp^{M_s*}}TiCl₃ on MAO-modified silica, bearing 4 wt % Al/SiO₂.⁴²

Grafted metal content

The effect of these preparative parameters was evaluated through an experimental design, which permits the optimization of the number of experiments and convenient access to the experimental uncertainties intrinsic to analytical data.³² For each variable, two levels were adopted : Zr or Ti, referring as the first catalyst grafted on the support (Cat I): (*i*BuCp)₂ZrCl₂ and {Tp^{M_s*}}TiCl₃, respectively; 373 or 723 K for silica thermal treatment temperature (T_{sup}), and 303 or 353 K for grafting temperature (T_{graft}). Table I shows the catalyst system preparation conditions and the resulting metal loading on silica determined by RBS and ICP-OES.

Considering grafted metal content determined by RBS and ICP-OES, a trend can be observed in which higher Zr contents were obtained when (*i*-Bu)₂ZrCl₂ was the first added catalyst, the support pretreatment temperature was 373 K, and the grafting took place at 303 K. In the case of {Tp^{M_s*}}TiCl₃, higher-grafted Ti

content was reached when this catalyst was first grafted, the pretreatment temperature was also the lowest one, but the grafting temperature was 353 K. Principal effects of each variable and interactions between them were calculated from RBS data from Table I and the results are shown in Table II. Considering that the concomitant effect of the three variables would be unlike, this value was employed to evaluate the effects.³² Concerning the catalyst addition order, independently of the addition sequence, Zr-grafted contents were always higher than Ti ones. This can be explained in terms of steric effect played by the coordination sphere in each metal center, in which a most steric demanding ligand is present in the case of {Tp^{M_s*}}TiCl₃. Regarding support pretreatment temperature, the increasing from 373 to 723 K impinges a reduction of ~60% of silanol groups.³⁷ This reduction is reflected in the resulting Zr content, which is decreased since there are lower available immobilization sites. On the other hand, such effect does not considerably influence the grafting of {Tp^{M_s*}}TiCl₃, in which the steric effect played by the ligands themselves seems to be the most relevant factor (Scheme 1).

Considering statistical significance at the 95% confidence level, two order effects were observed for the immobilization of the zirconocene: T_{sup} -Cat I and $T_{\text{graft}}-T_{\text{sup}}$. Such two order effects are irrelevant in the case of {Tp^{M_s*}}TiCl₃ grafting. Two order effects regarding the interaction between T_{graft} and Cat I were insignificant.

Catalyst activity in ethylene polymerization

The resulting catalysts were evaluated in ethylene polymerization. Table III shows catalyst activity and properties of the resulting polymers. Analysis of variance at the 95% confidence level did not allow to reveal any significant effect in catalyst activity. Nevertheless, the two most active catalysts were those that were prepared with the silica pretreated at 723 K. In the literature, higher catalyst activity were observed for silica pretreated at 723 K, in comparison to those thermally treated at 373, 473, or 573 K.³⁸ This behavior

TABLE III
Catalyst Activity in Ethylene Polymerization of the Supported Systems and Polymer Properties of the Resulting Polymers

Essay	Catalyst activity (10^5 g PE mol $^{-1}$ Mh $^{-1}$)	M_w (10^5 g mol $^{-1}$)	MWD	T_m (K)	χ (%)
1	2.4	3.3	2.0	408	39
2	0.7	3.7	2.3	408	39
3	2.9	2.8	2.1	408	45
4	4.8	2.9	2.2	409	46
5	2.7	2.5	2.1	409	47
6	3.5	2.5	2.3	409	40
7	6.7	2.7	2.3	408	47
8	3.3	3.0	2.1	409	42

Polymerization conditions: Al/M (Ti + Zr) = 2000; solvent: toluene; catalyst concentration: 10^{-6} mol L $^{-1}$.

was attributed to lower silanol density on the support surface, which may afford more horizontally spaced species, in which bimolecular deactivation reaction might be hampered. Besides, higher surface silanol densities might promote the generate of bidentate species (by consumption of both chloride from the zirconocene, for instance), which are inactive.³⁸

The nature of the surface species can be partially evaluated by the binding energy of the atom core level determined by XPS. XPS Zr 3d spectrum of the catalysts presented two signals due to the spin-orbital coupling of the 3d electrons of Zr: ~ 183.6 ($3d^{5/2}$) and ~ 186.0 ($3d^{3/2}$) eV. Ti 2p core level spectrum of the catalysts presents also a doublet centered at 458.5 and 464.0 eV due to spin-orbit coupling of the 2p electrons of Ti and can be attributed to $2p^{3/2}$ and $2p^{1/2}$ photoelectrons, respectively. Figure 1 represents the relationship between the catalyst activity and the energy of Zr $3d^{5/2}$ [Fig. 1(a)] and of Ti $2p^{3/2}$ [Fig. 1(b)].

In the case of Zr core level, the activity increases as the binding energy (BE) is reduced (Fig. 1(a)). The reduction in BE means that the Zr atoms are in an environment richer in electron density. Similar correlation was already reported in the literature.⁴³ On the other hand, no correlation could be drawn between catalyst activity and Ti $2p^{3/2}$ BE [Fig. 1(b)], suggesting that steric effects might be much more important for this catalyst species, or that the catalyst activity might mostly come from the Zr species. No correlations were observed concerning the BE of Cl (2p) or Al (2p).

Polymer properties

Table III presents also properties of the resulting polymers. Melting temperature was practically constant (408–409 K) being typical of high-density polyethylene. The degree of crystallinity ranges from 39 to 47%, being these values expected for polyethylene, which has a semicrystalline structure.

Attempts to determine M_w and MWD using standard GPC conditions (413 K) were unsuccessful. Such conditions were usually employed for polymers pro-

duced by homogeneous zirconocenes or supported ones.^{38–41} Analyses had to be performed under conditions employed for ultrahigh molecular weight de-

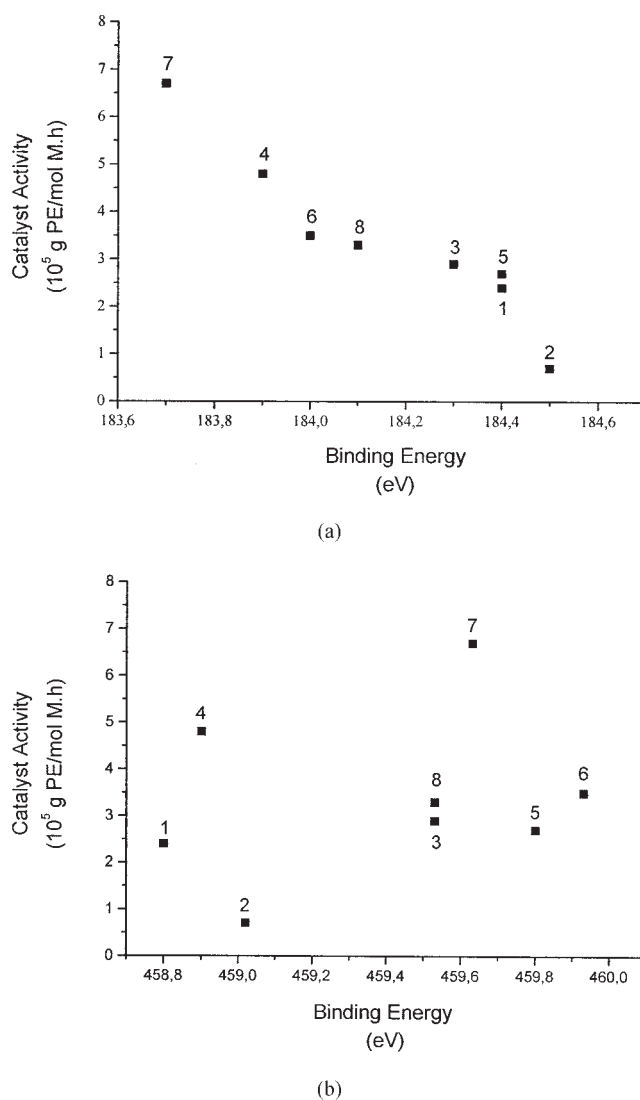


Figure 1 Relation between catalyst activity and binding energy (BE): (a) Zr ($3d^{5/2}$) and (b) Ti ($2p^{3/2}$) core level BE.

TABLE IV
Principal Effect of Each Variable and Interaction
Between Effects on M_w

Factor	Effect
T_{graft}	0.2341
T_{sup}	0.1683
CatI	-0.0346
(T_{graft} and T_{sup})	-0.2782
(T_{graft} and CatI)	0.0258
(T_{sup} and CatI)	0.5678
(T_{graft} and T_{sup} and CatI)	0.1229

termination (453 K). Under such conditions, all polymers were shown to be soluble. According to Table III, M_w remained comprised between 2.5×10^5 and $3.7 \times 10^5 \text{ g mol}^{-1}$. Although such values are lower than that corresponding to ultramolecular weight ($>1.5 \times 10^6$), they are higher than that usually observed in the case of $(i\text{BuCp})_2\text{ZrCl}_2$, homogeneous, supported on silica or on MAO-modified silica.⁴⁴ MWD remained around 2.0.

A first approach to data in Table III suggests that higher M_w were observed in systems in which [Ti] was first grafted and the supported pretreated at 373 K. Principal effects and interactions between effects were calculated for M_w and presented in Table IV.

According to Table IV, the addition order seems not to influence on the M_w , while increasing support pretreatment temperature or grafting temperature leads to an increase in M_w . Interaction effects could be observed in the case of interaction support pretreatment temperature and the two other variables. It is worth noting that in the case of the concomitant interaction of support pretreatment temperature and catalyst order, this is the most relevant effect, suggesting that one cannot interpret them separately.

Final remarks

Hybrid-supported catalysts prepared by sequentially grafting $(i\text{BuCp})_2\text{ZrCl}_2$ and $\{\text{Tp}^{\text{Ms}^*}\}\text{TiCl}_3$ on MAO-modified silica were shown to be active in ethylene polymerization. Analysis of resulting PE did not indicate bimodality or even a significant broadening in MWD. As already mentioned, one approach to afford polymers with bimodality consists in the use of two different catalyst center on the same support. If the chemical nature of the catalyst is extremely different, and therefore more prone to lead to polymer polydispersity, it is necessary that both catalyst centers work in comparable catalyst activity under the same polymerization conditions. Metallocene catalysts usually exhibit higher activity around 60°C. Nevertheless, Tp complexes show better activity at lower temperatures.^{7,21,45} Then, the polymerization temperature em-

ployed in the present study was suitable for the metallocene catalyst, but unfavorable for the Ti one.

The effect determined by the steric demanding ligand in Ti derivative plays an important role on the final grafted content. In such systems, zirconocene active species seems to play a major role in polymerization productivity as it was evidenced by XPS analysis, in which a correlation between Zr BE and catalyst activity could be observed.

Polymers obtained by supported zirconocenes, immobilized on MAO-modified silica (as in the present case), are known to present lower M_w than those produced by silica-based systems.^{22,44} In the present case, in spite of the presence of MAO species on silica surface, such hybrid systems produce polymers with even higher M_w in comparison to those observed for $(i\text{BuCp})_2\text{ZrCl}_2$ supported on bare silica. One cannot neglect the possibility that the Ti complexes (due to their steric demanding complexes) might be playing the role of spacers, hindering the deactivation step. Then, β -elimination transfer between two metallocene centers is hindered, resulting in a larger growth of the polymer chain, and on in higher molecular weight.⁴⁶

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