



Ethylene polymerization with catalyst systems based on supported metallocenes with varying steric hindrance

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Received 18 May 2003; received in revised form 18 May 2003; accepted 19 May 2003

Abstract

A series of metallocenes differing in the metal center ($M = \text{Zr, Ti, Hf}$), in the coordination sphere (RCp , with $R = \text{H, Me, } i\text{Bu, } n\text{Bu}$; Indenyl) and the bridge ($\text{Et, Me}_2\text{Si}$) were studied as homogeneous systems and supported on silica and MAO-mediated (2.0 wt.% Al/SiO_2) silica. The effect of these parameters were evaluated in the grafted metal content, in catalyst activity and in polymer properties. Metal content was determined by Rutherford backscattering spectrometry (RBS) and X-ray photoelectronic spectroscopy (XPS). Alkyl ligands seemed not to affect sensitively the final metal content, but indenyl complexes led to higher grafted metal content. Immobilization on MAO-mediated systems afforded higher metal contents. XPS measurements evidenced a reduction in Zr, Ti or Hf binding energy (BE) after immobilization on silica or on MAO-modified silica, in the latter two different species being observed after signal deconvolution. Monitoring of the surface reaction by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) showed that at this aluminum content residual silanol groups still remains, bearing probably two kind of species: one supported on silanol groups and another on MAO counterpart. Inductive effects from substituent on ligands influence in the catalyst activity, but this electronic effect is reduced in comparison to the steric effect played by the silica surface. Resulting polymers showed higher molecular weight than those produced by the soluble systems.

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Keywords: Ethylene polymerization; Supported metallocenes; XPS

1. Introduction

Polyethylenes produced by metallocene catalysts have a different architecture than conventional polyethylenes. Among the advantages of these systems, we can cite the differentiated properties of new resins, the adaptability of metallocene catalysts to existing plants, the potential for product/property modifications through rational catalyst manipulations, and an increasing pace of discovery through new re-

search methodologies. Using metallocene catalysts, it is possible for the first time to produce polyethylene, polypropylenes and copolymers with narrow molecular weight distribution, as well as, syndiotactic polypropylene and syndiotactic polystyrene, just to mention a few. Depending on the metallocene substituent pattern and symmetry, these catalysts permit a strong control of regio- and stereoregularities and of molecular weight distribution of homopolymers, as well as the synthesis of copolymers with a uniform comonomer distribution (see, for example, [1]).

A significant impediment to the commercialization of such catalysts is the cost reflected in the requirement

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that a very large excess of MAO must be employed to obtain high catalyst activity and catalyst stability. Moreover, besides the high amount of MAO, there are other disadvantages in the use of soluble metallocene catalyst. A solution polymerization process requires separation of the polymer, and removal, recovery and purification of the solvent. A gas-phase process is lower in cost and energy consumption by comparison.

An approach to overcome these problems has involved the heterogenization through adsorbing metallocenes on high surface area support. Moreover, as most of the existing polymerization plants run a slurry- and gas-phase process with heterogeneous catalysts, the homogeneous ones must be heterogenized on a support for the application in those process. Furthermore, the heterogenization of metallocene is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive swelling of polymers, and to produce polymer particles of a desired regular morphology.

Several kinds of supported metallocene catalyst systems have been reported, most of them employing silica as support, on which the metallocene is directly impregnated, or modified silica surface, or even on silica surface modified by silane coupling agents (see, for example, [2]).

The introduction of substituents at certain positions of the two aromatic ligands and/or the bridge modifies not only the steric and electronic conditions in the molecule but also the symmetry of such a metallocene dichloride complex. Concerning the nature of the coordination sphere of the metallocene, some works on the literature were devoted to study the effect of metallocene ligands on polymerization. The influence of the ring substituents has been already reviewed [3]. A systematic study employing 18 different kinds of substituted metallocenes in ethylene polymerization activated by MAO was performed evaluating the influence of the nature and of the size of the substituents on catalyst activity and on polymer properties [4]. However, a few work dealt with such effect involving supported metallocenes. For instance, Sacchi et al. [5] did a comparative study on propylene polymerization stereochemistry using the isospecific $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ (Et: Ethylene, Ind: Indenyl) and the aspecific $(\text{Ind})_2\text{ZrCl}_2$, both homogenous and supported on silica. Both supported systems produced

isospecific polymers, suggesting that only isospecific centers are formed independently of the metallocene stereochemical structure. A recent review was published by Alt and Köppl [6] comparing the behavior of more than 90 metallocene complexes in catalyst activity and in the resulting molecular weight, considering ethylene and propylene homopolymerization.

The present work aimed at studying the effect of the ligand hindrance in supported metallocene on the immobilized metal content, on catalyst activity and on polymer properties. The tested catalyst differed in the nature of alkyl substituent of the cyclopentadienyl (Cp) ring, in the presence or absence of ethylene bridge, in the metallic center and in the number of Cp substituent. The supported catalysts were prepared on Silica Grace 948 according to optimized previously developed preparative conditions [7]. Surface metal loadings were determined by the Rutherford backscattering spectrometry (RBS). Binding energy (BE) of the different metallocene species were measured by X-ray photoelectronic spectroscopy (XPS) and surface reactions were monitored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Catalyst activity was evaluated on ethylene homopolymerization having MAO as co-catalyst. For comparative reasons the corresponding homogeneous system were also tested. Polymers were characterized by their molecular weight, crystallinity, polydispersity, and melting (T_m) and crystallization (T_c) temperatures.

2. Experimental

2.1. Materials (chemicals)

Silica Grace 948 ($255 \text{ m}^2 \text{ g}^{-1}$) was activated under vacuum ($P < 10^{-4} \text{ mbar}$) for 16 h at 723 K. MAO (gently supplied by Witco, 10.0 wt.% toluene solution, average molar mass 900 g mol^{-1}) and the metallocenes (Witco or Boulder) were used without further purification. Ethylene, provided by COPESUL and argon were deoxygenated and dried through columns of BTS (gently supplied by BASF) and activated molecular sieve (13 \AA) prior to use. Pura grade toluene were deoxygenated and dried by standard techniques before use.

2.2. Preparation of supported catalysts

All grafting experiments were performed under inert atmosphere using the Schlenk technique. MAO-modified silicas were prepared by impregnation method containing 2.0 wt.% Al/SiO₂. Metallocene-supported catalysts were prepared by grafting method. In a typical experiment, for instance, an initial toluene solution of (nBuCp)₂ZrCl₂ corresponding to 1.5 wt.% Zr/SiO₂ was added to bare or MAO-treated silica, and the resulting slurry was stirred for 1 h at 353 K, and then filtered through a fritted disk. The resulting solids were washed with 12 × 2.0 cm³ of toluene and dried under vacuum for 4 h. Detailed description of the immobilization procedures are reported elsewhere [7–9].

2.3. Characterization of supported catalysts

2.3.1. Rutherford backscattering spectrometry

Zirconium loadings in catalysts were determined by RBS using He⁺ beams of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. During analysis, the base pressure in the chamber is kept in the 10⁻⁷ mbar range using membrane (to prevent oil contamination of the sample) and turbodrag molecular pump. The method is based on the determination of the number and the energy of the detected particles which are elastically scattered in the Coulombic field of the atomic nuclei in the target. In this study, the Zr/Si atomic ratio was determined from the heights of the signals corresponding to each of the elements in the spectra and converted to wt.% Zr/SiO₂. For an introduction to the method and applications of this technique the reader is referred elsewhere [10,11].

2.3.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were obtained on a PHI 5600 Esca System (Φ Physical Electronics), using monochromated Al Kα radiation (1486.6 eV). Spectra were taken at room temperature in low resolution (pass energy 235 eV) in the range of 1000–0 eV binding energy and in high-resolution (pass energy 23.5 eV) modes for the Si 2p, Al 2p and Zr 3d regions. Resolution was 0.05 eV.

Samples were mounted on an adhesive copper tape. They were prepared in a glove box, transferred under

nitrogen atmosphere and then evacuated until reaching 10⁻⁶ mbar by a turbomolecular pump in an introduction chamber. During data collection, the ion pumped chamber was maintained at 5 < 10⁻⁹ mbar. Takeoff angles (angle between the surface plane and the detector) was 75° in the XPS experiment. Normally 50 scans were signal averaged for selected binding energy windows and processed by the software supplied by the manufacturer. Current of the electron gun (neutralizer) was 21.5 mA.

Binding energies examined (element, transition, approximate binding energy, and range scanned) were as follows: Si 2p, 103.3 and 96–108 eV; Al 2p, 72.9 and 70–80 eV; and Zr 3d^{5/2}, 178.9 and 176–188 eV. In the case of silica-supported systems, all binding energies values were charge referenced to the silica Si 2p at 103.3 eV. Otherwise, they were referenced to the Au 4f^{7/2} peak at 84.0 eV.

Estimation of surface atomic ratios was based on 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.

Three measurements per sample were performed, and the reproducibility of the XPS analysis was confirmed. For each of the XPS spectra reported, an attempt has been made to deconvolve the experimental curve in a series of peaks that represent the contribution of the photoelectron emission from atoms in different chemical environments. These peaks are described as having Gaussian and Lorentzian contributions in order to take into account the effects of the instrumental error on the peak shape characteristic of the photoemission process.

2.3.3. Diffuse reflectance infrared spectroscopy

The solid catalysts were analyzed as powder in a DRIFT accessory, equipped with sampling cup. The spectra were recorded at room temperature on a Bomem MB-102 Spectrometer, coadding 36 scan at resolution of 4 cm⁻¹. This study was restricted to the mid-IR region (4000–1100 cm⁻¹) due to strong bulk absorption of silica in low wavenumber region. The spectra were collected as reflectance units and transformed to Kubelka-Munk (KM) units. All the measurements were performed at nitrogen atmosphere.

2.4. Polymerization reactions

Polymerizations 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 monomers. For each experiment, a mass of catalyst system corresponding to 10⁻⁵ mol l⁻¹ of Zr 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 at Al/Zr = 2000, using MAO as co-catalyst. 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.

2.5. Polyethylene characterization

Molar masses and molar mass distributions were investigated with a Waters CV plus 150C high-temperature GPC instrument, equipped with viscosimetric detector, and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limit 1 × 10⁷ for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1 cm³ 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.

Polymer melting points (*T*_m) and crystallinities (*χ*_c) were determined on a Polymer Laboratories differential scanning calorimeter (DSC) calibrated with Indium, using a heating rate of 10 K min⁻¹ in the temperature range 303–423 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.

3. Results and discussion

3.1. Metal catalyst loading

In a previous work we studied the influence of some experimental parameters in the immobilization of (*n*BuCp)₂ZrCl₂ on silica [12]. Higher metal loadings and catalyst activities were achieved when silica was

Table 1

Metal loading on silica and MAO-modified silica-supported metallocene systems determined by RBS (M = Ti, Zr, Hf)

Metallocene	M/SiO ₂ (wt.%)	M/MAO/SiO ₂ (wt.%)
Cp ₂ TiCl ₂	0.4	0.5
Cp ₂ ZrCl ₂	1.0	1.3
(MeCp) ₂ ZrCl ₂	1.0	1.4
(<i>i</i> BuCp) ₂ ZrCl ₂	0.8	1.1
(<i>n</i> BuCp) ₂ ZrCl ₂	0.8	1.2
Et(Ind) ₂ HfCl ₂	1.2	1.1
Et(Ind) ₂ ZrCl ₂	1.5	2.5
Et(IndH ₄) ₂ ZrCl ₂	0.7	0.9
Me ₂ Si(Ind) ₂ ZrCl ₂	0.7	0.8
CpTiCl ₃	1.1	nd

nd: not determined.

thermally treated at 723 K under vacuum, and grafting was performed at 353 K for 1 h. Concerning the modification of silica with MAO, adsorption isotherms measurements showed that silica surface saturation is achieved at ca. 8.0 wt.% Al/SiO₂ [8]. Therefore, we chose 2.0 wt.% Al/SiO₂ content, which represented aluminum concentration below its saturation level on silica surface.

Table 1 represents the immobilized metal content on silica and on MAO-modified silica for the different studied supported metallocenes. The metallocene catalysts listed in Table 1 can be grouped into three families: the cyclopentadienyl ring metallocene [Cp₂TiCl₂, Cp₂ZrCl₂, (MeCp)₂ZrCl₂, (*i*BuCp)₂ZrCl₂, (*n*BuCp)₂ZrCl₂], the *ansa*-metallocene [Et(Ind)₂HfCl₂, Et(Ind)₂ZrCl₂, Et(IndH₄)₂ZrCl₂, Me₂Si(Ind)₂ZrCl₂] and the monocyclopentadienyl metallocene (CpTiCl₃).

The final metal loading varied from 0.4 to 1.5 wt.% M/SiO₂ (M = Ti, Zr, Hf) and from 0.5 to 2.5 wt.% M/MAO/SiO₂ (M = Ti, Zr, Hf). In almost all the cases, the immobilization of the metallocene on the MAO-modified silica led to higher metal content in comparison to direct grafting on silica. Similar results were also reported in [13].

The differences observed in the resulting metal content can be discussed according to some catalyst characteristics. Considering the metal center in catalysts having the same coordination sphere (Cp₂ZrCl₂ and Cp₂TiCl₂; Et(Ind)₂ZrCl₂ and Et(Ind)₂HfCl₂), we observe that zirconocene led to higher grafted content than titanocene or hafnocene. Taking into account the

atomic radius of the three elements, Ti (1.45 Å), Zr (1.60 Å) and Hf (1.59 Å) [14], the less steric effect played by the titanium atom should lead to the highest grafted metal content. The lowest observed metal content attained in the case of titanocene could be in part explained by its lower thermal stability [15]. Nevertheless, we performed the grafting reaction at 298 K, but the grafted metal content showed no difference in Ti content, comparing to that prepared at 353 K.

Comparing hafnocene with zirconocene, the former led to a slightly lower metal content in spite of similarity in their atomic radius. Grafting on MAO-modified silica seems not to enhance the final metal content in the case of the $\text{Et(Ind)}_2\text{HfCl}_2$, while an increase of ca. 60% occurred in the case of $\text{Et(Ind)}_2\text{ZrCl}_2$.

Concerning the coordination sphere, two aspects should be taken into account: the presence/absence of the bridging unit and the ligands. Considering the studied catalysts, the highest grafted metal content was achieved in the case of $\text{Et(Ind)}_2\text{ZrCl}_2$. The rigid ligand framework provided by the bridging unit might reduce the molecule dynamic volume decreasing in turn steric effects during the surface reaction. Similar metal contents were mentioned in the literature. The immobilization of the same metallocene carried on 343 K in toluene for 16 h was shown to graft 1.35 and 1.42 wt.% Zr/SiO₂ for $\text{Et(Ind)}_2\text{ZrCl}_2$ and $(\text{Ind})_2\text{ZrCl}_2$, respectively [5]. Other authors mentioned similar results: 1.53 wt.% Zr/SiO₂ for $\text{Et(Ind)}_2\text{ZrCl}_2$ using silica dehydrated at 833 K, and grafting performed for 18 h at 343 K [16]. Kaminsky and Renner found 1.45 wt.% Zr/SiO₂, grafting $\text{Et(Ind)}_2\text{ZrCl}_2$ for 16 h at 343 K, followed by Soxhlet extraction with toluene for 2 days [17]. It is worth citing that the grafting of $\text{Ind}_2\text{ZrCl}_2$ on silica at 323 K for 5 h was already reported to afford no retained zirconocene after washing the solid with toluene [18].

As we can see from Table 1, high metal content was also observed in the case of $\text{Et(Ind)}_2\text{HfCl}_2$. Nevertheless, in the case of the two other tested *ansa*-metallocene, lower metal contents were achieved. For $\text{Et(IndH}_4\text{)ZrCl}_2$, the hydrogenation of the six-member ring led to an aromaticity loss, rendering it more closely related to the substituted Cp complexes. Similar behavior was reported by Collins et al. [19], where on a partially dehydroxylated silica $\text{Et(Ind)}_2\text{ZrCl}_2$ and $\text{Et(IndH}_4\text{)}_2\text{ZrCl}_2$ were grafted in 1.47 and 0.67 wt.% Zr/SiO₂, respectively. In the case

of $\text{Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$, the presence of a dimethylsilyl bridging unit might afford electronic and steric differences in comparison to $\text{Et(Ind)}_2\text{ZrCl}_2$. The Me_2Si bridge render a bigger bite angle between the two Ind unities than Et one. Moreover, this bridging unit shifts the electronic density toward the Si atom, reducing the donation effect of the Ind groups to Zr [20]. The less positive charge on the central atom might influence the catalyst reaction with the surface during the grafting reaction.

Taking into account the cyclopentadienyl group, it was found that the metal loading was considerably influenced by the size of the alkyl substituent on the cyclopentadienyl ring. Tait and Monteiro [21] achieved under similar conditions (silica dehydroxylated at 723 K and grafting performed at 343 K) 2.5 wt.% Zr/SiO₂ for Cp_2ZrCl_2 , while Sacchi et al. [5] obtained 0.60 wt.% Zr/SiO₂ for the same catalyst, also under similar experimental conditions.

The introduction of a methyl into the Cp group does not influence the grafted metal content. The introduction of larger groups such as *n*Bu or *i*Bu led to a lower metallocene immobilization. Nevertheless, between both ligands there is no difference in the final metal content.

The mono Cp metallocene grafted 1.1 wt.% Ti/SiO₂. Comparing to Cp_2TiCl_2 , the mono Cp complex indeed lead to higher grafted metal content due to less steric effect played by the coordinate sphere. Nevertheless the grafted content is still lower than the studied *ansa*-metallocene catalysts. As already discussed, this can be in part resultant from the lower thermal stability of titanocenes. Soga et al. [22] prepared $\text{CpTiCl}_3/\text{SiO}_2$ at 383 K for 3 h, obtaining 0.63% Ti/SiO₂.

XPS analysis can also provide the surface composition of the catalysts. The catalyst surface composition of some of the supported catalysts are represented in Table 2. Catalyst grafting takes place preferentially at the external surface of the silica grains. Comparing data of Table 2 with Table 1, values measured by RBS are systematically lower than those obtained by XPS. In the case of RBS, assuming that silica is in its crystalline form (α -quartz), the reach of 2.0 MeV He⁺ ions in the support would be 8% of the first grain analyzed by RBS ($\approx 6 \mu\text{m}$). On the other hand, the XPS measurable region is estimated roughly as 5 nm in depth. Therefore, XPS is more sensible to the uttermost

Table 2

Metal loading on silica and MAO-modified silica-supported metallocene systems determined by XPS (M = Ti, Zr, Hf)

Metallocene	M/SiO ₂ (wt.%)	M/MAO/SiO ₂ (wt.%)	
		M/SiO ₂	Al/SiO ₂
Cp ₂ TiCl ₂	2.0	3.5	0.2
Cp ₂ ZrCl ₂	1.3	4.8	0.1
(MeCp) ₂ ZrCl ₂	1.4	2.9	0.2
(<i>i</i> BuCp) ₂ ZrCl ₂	1.1	4.5	0.2
(<i>n</i> BuCp) ₂ ZrCl ₂	1.2	4.9	0.2
Et(Ind) ₂ HfCl ₂	1.3	2.0	0.3
Et(Ind) ₂ ZrCl ₂	4.7	15.6	0.6
Et(IndH ₄) ₂ ZrCl ₂	1.1	2.1	0.2
Me ₂ Si(Ind) ₂ ZrCl ₂	2.0	2.8	0.1
CpTiCl ₃	3.1	nd	nd

nd: not determined.

surface composition, where the relative contribution of Zr, Ti or Hf atoms is much more important. In spite of the numeric differences between both techniques, grafted metal content showed the same trend among the different supported catalysts. The low values for Al content suggest that MAO must be not so much exposed on the silica grain, since the support was first reacted with MAO, and then with the metallocenes.

3.2. Metallocenes' binding energy

Zr 3d core level spectrum is characterized by the presence of two signals due to spin-orbit coupling of the 3d electrons of Zr: ca. 183 (3d^{5/2}) and 185 eV (3d^{3/2}). Typical zirconocene XPS spectra has been published elsewhere [23]. After immobilization on silica surface or on MAO-modified silica surface, deconvolution of the resulting spectra suggests the presence of two species.

Table 3 reports the BE of the neat metallocene and the supported systems resulting on silica and on MAO-modified silica. For the sake of simplicity we present only the 3d^{5/2} (Zr), 2p^{3/2} (Ti) or 4f^{7/2} (Hf) signals. The BE of Cp₂ZrCl₂ was reported in the literature as 181.7 eV [24], while of Et(Ind)₂ZrCl₂, 182.0 eV [25]. In the homogeneous catalysts, higher alkyl donor ligands (*i*Bu and *n*Bu) induce a reduction in the Zr 3d^{5/2} BE as compared to the Me one, corresponding to an increase of electronic density on the metal atom. Considering the indenyl systems, the hydrogenation of the indenyl ring leads to a reduction in the resulting

Table 3

Binding energy (BE) of some metallocene compounds: neat, supported on silica and on MAO-modified silica

Metallocene	Neat (eV)	M/SiO ₂ (eV)	M/MAO/SiO ₂ (eV)
Cp ₂ ZrCl ₂	182.0	183.1	182.9 (30) 184.5 (70)
(MeCp) ₂ ZrCl ₂	182.0	181.4 (49) 183.0 (51)	182.9 (32) 183.6 (68)
(<i>i</i> BuCp) ₂ ZrCl ₂	181.7	183.2	181.6 (35) 183.0 (65)
(<i>n</i> BuCp) ₂ ZrCl ₂	181.6	182.4	182.3 (32) 183.9 (68)
Et(Ind) ₂ ZrCl ₂	182.4	180.4 (22) 182.6 (78)	182.5 (30) 183.7 (70)
Et(IndH ₄) ₂ ZrCl ₂	181.7	181.3 (43) 183.2 (57)	182.0 (32) 183.8 (68)
Me ₂ Si(Ind) ₂ ZrCl ₂	182.7	182.8	182.0 (39) 183.7 (61)
Et(Ind) ₂ HfCl ₂	15.5	16.6 18.0	15.7 17.3
CpTiCl ₃	457.7	458.8	nd
Cp ₂ TiCl ₂	457.2	458.4	458.9

Values in parentheses are percentages. nd: not determined.

BE in accordance to the expected resulting alkyl character. On the other hand, the presence of methylsilyl bridge displaces the electronic density toward the Si atom, reducing the donating effect from the Ind ligand to the Zr atom. Therefore, the Zr BE is shifted to higher values. In the case of the titanocenes, the replacement of one chloride by one Cp ligand results in greater electron donation to the titanium and, as a result, in a net reduction in BE as observed in Table 3.

Taking into account the BE of the resulting metallocene catalysts grafted on silica, we observed the generation of species having BE higher than that observed on the neat compound. The shift to higher BE indicates the presence of a more electron deficient species, and this can result from the exchange between chlorine atom and oxygen from silica, the latter being more electronegative. Similar behavior is reported in the literature for Et(Ind)₂ZrCl₂, which BE shifts from 182.0 eV (neat complex) to 182.7 eV (supported on silica) [26]. In some systems, two signals for 3d^{5/2} were observed in the case of some zirconocene, suggesting the existence of two different sites, but no clear

relationship between structure of the metallocene and number of species on the surface could be established.

It is worth noting that in the case of silica-supported catalyst, in the case of existence of two signals, one is slightly lower in energy than the homogeneous catalysts and the other at a higher BE. Nevertheless, in the case of MAO-supported catalyst, most of the systems (excepting $\text{Cp}_2\text{TiCl}_2/\text{MAO}/\text{SiO}_2$ system) showed the presence of two signals, both new signals being at BE higher than that of the neat compounds. The shift toward higher BE represents an environment electronically deficient (more *cationic*). It is believed that the immobilization of the metallocene on the MAO-modified silicas proceeds through extraction of chloride by the anchored MAO forming a “cation-like” metallocenium active species, which would explain the presence of high BE species.

Atiquilah et al. [25] observed also the presence of two species when $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ was immobilized on MAO-modified silica: 182.8 and 183.9 eV (both values reported for Zr $3d^{5/2}$ signal). The lower BE species is attributed to a zirconocenium ion-pair $[\text{SiO}]^- [\text{Et}(\text{Ind})_2\text{ZrCl}]^+$ originated from the reaction between the metallocene and silanol groups from the silica surface, while the higher one, to the zirconocenium methylated species stabilized in multi-coordinative crown aluminoxane species. In fact, according to Table 3, the lowest BE species is minority suggesting that it might be generated from the reaction with residual silanol groups.

3.3. Surface silanol groups

In previous study we have observed that during MAO impregnation up to 8–10 wt.% Al/SiO₂ there is still residual OH groups on silica surface [26]. We have monitored the stepwise preparation of the supported catalysts by DRIFTS. After thermal treatment, silica infrared spectrum is characterized by a band at 3744 cm^{-1} attributed to isolated silanol groups. After 2 wt.% Al/SiO₂ impregnation (MAO treatment), two bands (2973 and 2959 cm^{-1}) are detected and attributed to methyl groups. Nonetheless, there is still non-consumed silanol groups. In order to evaluate the number of silanol groups consumed during the surface reaction, we correlated the silanol band (3744 cm^{-1}) area with an invariable band at 1867 cm^{-1} (internal standard) attributed to overtone structure vibration

Table 4
Residual silanol content after zirconocene grafting

Catalyst	Zr/MAO/SiO ₂ ^a (%)	Residual SiOH (a.u.)
Cp_2ZrCl_2	1.3	0.12
$(i\text{BuCp})_2\text{ZrCl}_2$	1.1	0.04
$(n\text{BuCp})_2\text{ZrCl}_2$	1.2	0.02
$(\text{MeCp})_2\text{ZrCl}_2$	1.4	0.15
$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	2.5	0.21
$\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$	0.9	0.03
$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$	0.8	0.23

^a Determined by RBS.

[27]. Table 4 reports the rate of consumed silanol groups. The $(i\text{BuCp})_2\text{ZrCl}_2$, $(n\text{BuCp})_2\text{ZrCl}_2$ and $\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$ shows similar metal grafted content and consumed OH group rate. Similar results are observed between $(\text{MeCp})_2\text{ZrCl}_2$ and Cp_2ZrCl_2 . $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$, in spite of presenting different metal content, show similar consumed OH groups. This result suggests that in fact, the reduction in isolated silanol band might indicate that these groups could be affected by the grafted metallocene by intermolecular interactions, reducing therefore the intensity of the isolated silanol band.

3.4. Catalyst activity

The supported system were evaluated in ethylene polymerization, using external MAO as co-catalyst (Table 5).

Concerning the metal center, zirconocenes showed the highest activities. Kaminsky et al. [28] comparing

Table 5
Catalyst activity in ethylene polymerization

Metallocene	Catalyst activity ($10^5\text{ g PE mol Zr}^{-1}\text{ h}^{-1}$)		
	Homogeneous	M/SiO ₂	M/MAO/SiO ₂
$(\text{MeCp})_2\text{ZrCl}_2$	181.0	58.3	91.8
$(i\text{BuCp})_2\text{ZrCl}_2$	83.9	52.8	23.9
$\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$	80.7	28.8	43.2
$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	77.0	Traces	4.9
$(n\text{BuCp})_2\text{ZrCl}_2$	73.4	26.0	48.9
$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$	67.8	Traces	Traces
Cp_2ZrCl_2	57.5	27.6	54.0
Cp_2TiCl_2	25.1	10.0	15.3
$\text{Et}(\text{Ind})_2\text{HfCl}_2$	5.4	Traces	Traces

Temperature: 333 K; Al/Zr = 2000; $[\text{M}] = 10^{-5}\text{ mol l}^{-1}$; reaction time: 30 min. M = Zr, Ti, Hf.

Et(Ind)₂ZrCl₂ and Et(Ind)₂HfCl₂ observed that both in ethylene and propylene homopolymerization, hafnocene showed much lower catalyst activity. This behavior was attributed to different concentration of active sites and differences in the metal–carbon bonding force, besides the atom size. Cp₂TiCl₂ showed lower activity than Cp₂ZrCl₂, probably due to lability of the former at higher temperatures [15].

Electronic and steric factors of the ligands affect the catalyst activity. Ewen [29] and Chien and Wang [30] studied the effect of alkyl substituents in Cp rings. The following order was observed: (MeCp)₂ZrCl₂ > (EtCp)₂ZrCl₂ > Cp₂ZrCl₂ > (Me₅Cp)CpZrCl₂ > (Me₅Cp)₂ZrCl₂. Alkyl ligands play an electron donating effect of alkyl group toward the zirconium metal.

Concerning the Cp systems, we can observe the following order among the homogeneous systems: MeCp > *i*BuCp > *n*BuCp > Cp. The presence of alkyl indeed increase the catalyst activity. Nevertheless, the steric effect played by bulkier ligands (*i*Bu and *n*Bu) might afford a relatively little opposing effect to the electron donating one in ethylene coordination leading to a reduction in catalyst activity in comparison to MeCp ligand. Among the Indenyl complexes, that bearing a methylsilyl bridge due to its more electropositive character attracts the electron density, reducing the donating effect to the ligands, increasing therefore the electron deficiency on the metal center. For that reason, the interaction between the olefin and the catalyst center might increase, reducing the rate in the coordination and polymer chain insertion steps, leading in turn to a decrease in catalyst activity.

In the case of supported catalysts, the silica surface played the role of a huge bulky ligand. In both M/SiO₂ and M/MAO/SiO₂ we observe a reduction in catalyst activity. This fact may be attributed the steric effect played by the silica surface, which acts as a huge bulky ligand. Moreover, not all the supported metal content corresponds to active species. It is believed that only ca. 1% of the silica-supported metallocene affords active species [13]. According to Table 5, it seems that in some cases the steric effect played by the support is preponderant over the electronic effect (compare, for instance, data from Cp₂ZrCl₂ and (*n*BuCp)₂ZrCl₂). Indenyl ligand complexes showed very low catalyst activity.

Comparing the supported systems, in the case of the MAO-mediated ones, the catalyst systems were shown

to be more active than those produced on bare silica. This fact has been reported in the literature and attributed to generation of cationic species, which floats over the MAO stabilizing coverage [16]. Besides, desorption of the metallocene due to the leaching of the weakly anchored active species by external MAO has been observed, producing certain amount of soluble species. The polymerization takes place partially in solution and partially on the support [13].

Attempts to correlate Zr BE and catalyst activity did not showed any clear trend, probably due to steric effects played by the coordinative sphere which might also influence on the polymerization reaction.

3.5. Polymer properties

All systems produced polyethylenes with melting (*T*_m) and crystallization (*T*_c) temperatures practically constant at 408.5 ± 0.7 and 392.0 ± 1.0 K, respectively. These temperatures are typical of linear high-density polyethylenes.

Table 6 presents weight average molecular weight (*M*_w) and polydispersity index (*M*_w/*M*_n) of the polyethylenes produced with the different homogeneous and supported systems. According to Table 6 all the polymers produced with the supported catalysts present a higher molecular weight than that obtained with the soluble system. This behavior has already been observed [7,12] and attributed to blocking of one of the sides of polymerization active sites by the support, hindering the deactivation step. In other words, β-elimination transfer between two metallocene centers is hindered, resulting in a larger growth of the polymer chain, and so in higher molecular weight [17]. It is worth mentioning that polymers with high

Table 6
Molecular weight and polydispersity index of homogeneous and supported systems

Metallocene	<i>M</i> _w / <i>(M</i> _w / <i>M</i> _n) (10 ⁵ g mol ⁻¹)		
	Homogenous	M/SiO ₂	M/MAO/SiO ₂
(MeCp) ₂ ZrCl ₂	0.4 (2.0)	1.5 (3.4)	1.4 (2.4)
Cp ₂ ZrCl ₂	0.1 (2.6)	0.9 (2.8)	0.6 (2.5)
(<i>n</i> BuCp) ₂ ZrCl ₂	0.8 (2.5)	1.5 (2.4)	1.2 (2.4)
Et(IndH ₄) ₂ ZrCl ₂	0.8 (2.0)	2.2 (2.2)	2.0 (2.5)
(<i>i</i> BuCp) ₂ ZrCl ₂	1.0 (2.5)	1.4 (2.9)	1.2 (2.5)
Et(Ind) ₂ ZrCl ₂	1.9 (2.0)	–	2.2 (2.4)

average molecular weights show better mechanical properties as compared with those with low average molecular weights.

Polydispersity values remained around 2.5. No bimodality was observed. It seems that the single site nature of the homogeneous catalyst is kept on the surface.

4. Conclusion

In supported metallocenes, the final grafted content depends on the metal center ($\text{Ti} < \text{Hf} < \text{Zr}$), on the coordination sphere and on the support. In the case of Cp ligands the presence of alkyl substituent does not impinge a significant effect. However, indenyl derivatives lead to higher metal content. The presence of Me_2Si bridge reduced the final grafted content in comparison to ethylene one. Higher metal contents were achieved in the case of MAO-mediated systems. In this case, two surface species were observed by XPS analysis probably one resulting from the reaction between metallocene and surface silanol groups and other from the reaction with immobilized MAO. In homogeneous systems the inductive effect from alkyl groups can be observed, but this effect is reduced in supported systems probably due to the steric effect played by the silica surface, which seems to be much more important than the metallocene coordination sphere itself. Besides, a reduction in catalyst activity itself is observed in all the supported systems in comparison to the homogeneous counterpart. Concerning polymer properties, the supported systems presented higher molecular weight in comparison to those obtained with the homogeneous counterpart.

Acknowledgements

This work was partially supported by the Brazilian agencies CNPq and FINEP/PADCT III. Financial support for Prof. J.H.Z. dos Santos has been provided by the Japan Society for Promotion of Science (JSPS).

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