

# Influence of PMHS loading on the silica surface, on catalyst activity and on properties of resulting polymers

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## Abstract

The homopolymerization of ethylene was investigated using the catalysts of  $(n\text{BuCp})_2\text{ZrCl}_2$  supported on PMHS-modified silicas (PMHS = polymethylhydrosiloxane). The effect of the amount of the organosilane polymer on the metallocene grafted content was studied in loadings of PMHS from 0.0 to 3.0 wt.% Si/SiO<sub>2</sub>, in which the grafted Zr content was from 0.9 to 0.3 wt.% Si/SiO<sub>2</sub>. The metal contents were determined by Rutherford backscattering spectrometry (RBS), while the catalyst stepwise preparation was monitored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The chemical environment of the zirconocene surface species were further probed by X-ray spectroscopy (XPS) and the metal distribution was studied by Electron probe microanalysis (EPMA). These catalyst systems produced polyethylenes with a narrow molecular weight distribution using methylaluminoxane as co-catalyst, and their catalyst activities were three times greater than the one obtained with  $(n\text{BuCp})_2\text{ZrCl}_2$  supported on the bare SiO<sub>2</sub>. Effects of the support structure and the chemical modification on the catalyst performance are presented and discussed.

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## 1. Introduction

Metallocenes as the olefin polymerization catalysts have been at the center of the attention in the past 10 years and been increasing their importance as new catalysts to produce polymers with unique properties and with market share potentials [1]. Nevertheless, from the large scale industrial point of view it is extremely important to develop the heterogeneous catalysts for the gas phase and the slurry polymerization in order

to apply them to the well-established industrial plant (*drop-in* technology), and the additional advantage is the fact that the heterogeneous catalysts can control the morphology of the polymer formed [2].

Various heterogeneization approaches have been cited in the literatures and most of them have been employing the high surface area silicas [3]. In addition to the control of the polymer morphology, silica's unique surface chemistry, namely the concentration and the strength of hydroxyl groups and siloxane bridges, can be utilized to anchor and disperse the reagents used in the organometallic catalysts. However, the immobilization process seems not to be simple, since some intrinsic undesirable properties,

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such as the acidity of various surface OH groups can lead to the formation of the multiple active sites, the catalyst deactivation and the leaching. Besides such a catalyst deactivation, the huge steric effect played by the support itself on the accessibility to the catalyst center contributes to a decrease in the catalyst activity. Many efforts have been made in order to generate the active supported metallocene species which are more active, more stable and less prone to leaching. Among these approaches we can cite the use of the surface spacers [4], the use of in situ impregnation [5] and the synthesis of the supported metallocene from the sol–gel method [6].

In a previous study, we evaluated the role of various organosilicon compounds differing in the coordination sphere as the silica modifiers [7]. The resulting supports were employed for  $(n\text{BuCp})_2\text{ZrCl}_2$  grafting and this supported catalysts exhibited two times of the activity compared to that of the same metallocene supported on the bare silica. The increase in activity was attributed to the generation of the catalysts species having more space on the silica surface by the previous consumption of the silanol groups through reaction with the organosilanes. The role of the organosilanes as the horizontal spacers was later confirmed by the molecular modeling [8].

In the present study, we investigated the effect of polymethylhydrosiloxane (PMHS) on the modification of the silica surface in the range of PMHS contents from 0.0 to 3.0 wt.% Si/SiO<sub>2</sub>. Then the modified silicas were reacted with  $(n\text{BuCp})_2\text{ZrCl}_2$ . The metal loadings were determined by Rutherford backscattering spectrometry (RBS) and the surface reactions were monitored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The binding energies of the surface species were measured by X-ray photoelectron spectroscopy (XPS), while the spatial distribution of the zirconocenes on the support grains was obtained by electron probe microanalysis (EPMA). The catalyst systems were tested in the ethylene polymerization using methylaluminoxane (MAO) as co-catalyst. Effects of the contents of PMHS modifier on the silica surface were evaluated on the grafted metal content, on the catalyst activity and on the polymer properties such as the molecular weight, the crystallinity, the polydispersity index, and the melting and the crystallization temperatures. For comparative reasons, the homogeneous systems were equally tested.

## 2. Experimental

### 2.1. Materials

Silica Grace 948 (255 m<sup>2</sup> g<sup>-1</sup>; mean pore diameter: 248 Å) was activated under vacuum ( $P < 10^{-5}$  mbar) for 16 h at 450 °C. MAO (gently supplied by Witco, 10.0 wt.% toluene solution, average molar mass 900 g mol<sup>-1</sup>),  $(n\text{BuCp})_2\text{ZrCl}_2$  (Witco) and polymethylhydrosiloxane (Aldrich;  $M_w = 2210$  Da), were used without further purification. Ethylene, provided by COPESUL and argon (White Martins) were deoxygenated and dried through columns of BTS (generous supplied by BASF) and activated molecular sieve (13 Å) prior to use. Pure grade toluene were deoxygenated and dried by standard methods before use.

### 2.2. Preparation of supported catalysts

All grafting experiments were performed under the inert atmosphere using the Schlenk technique. The PMHS-modified silicas were prepared by impregnating PMHS using 1.0 g of the activated silica with a toluene solution of PMHS corresponding to 0.15–3.00 wt.% Si/SiO<sub>2</sub>, at room temperature for 30 min. The solvent was removed under vacuum, then a toluene solution of  $(n\text{BuCp})_2\text{ZrCl}_2$  corresponding to 1.5 wt.% Zr/SiO<sub>2</sub> was added and the resulting slurry was stirred for 1 h at room temperature, and then filtered through a fritted disk. The resulting solids were washed 15 times with 2.0 cm<sup>3</sup> of toluene and dried under vacuum for 4 h.

### 2.3. Characterization of supported catalysts

#### 2.3.1. Rutherford backscattering spectrometry (RBS)

Zirconium contents in catalysts were determined by RBS using He<sup>+</sup> beams of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. During the analysis the base pressure in the chamber is kept in the 10<sup>-7</sup> mbar range using the membrane (to prevent oil contamination of the sample) and the molecular turbodrag 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/SiO<sub>2</sub>. For an introduction to the method and applications of this technique the reader is referred elsewhere [9,10].

### 2.3.2. Diffuse reflectance infrared spectroscopy (DRIFTS)

The solid catalysts were analyzed as compressed powders in a DRIFTS accessory, equipped with a sampling cup. The spectra were recorded at room temperature on a Bomem MB-102 spectrometer, co-adding 36 scans at resolution of 4 cm<sup>-1</sup>. This study was restricted to the mid-IR region (4000–1100 cm<sup>-1</sup>) due to strong bulk absorption of the silica in low wavenumber region. So that the discussion of spectra was limited to the 4000–2000 cm<sup>-1</sup> region, where OH, CH and SiH stretchings can be observed. Spectra were collected in reflectance units and transformed to Kubelka–Munk (KM) units. All the measurements were performed under the nitrogen atmosphere.

### 2.3.3. X-ray photoelectron spectroscopy (XPS)

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 using a pass energy of 23.5 eV for the Si (2p) and Zr (3d) regions. Spectral 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<sup>-6</sup> mbar by a turbomolecular pump in an introduction chamber. Afterwards, they were transferred to the analysis chamber where the base pressure, during data collection was maintained lower than 5 × 10<sup>-11</sup> Pa. Takeoff angles (angle between the surface plane and the detector) of 45, 60 and 75° were used to control the sampling depth. Normally 50 scans were signal averaged for selected binding energy windows and processed by the software supplied by the manufacturer. All binding energies values were charge referenced to the silica Si 2p at 103.3 eV. Current of the electron gun (neutralizer) was 21.5 mA.

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 contri-

bution of the photoelectron emission from atoms in different chemical environments. These peaks are described as having Gaussian (ca. 80%) and Lorentzian contributions (in order to take into account the effects of the instrumental resolution on the peak shape).

### 2.3.4. Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA)

SEM and EPMA experiments were carried out using a JEOL JXA-8900L WD/ED combined with microanalyzer. The catalysts were initially fixed on a carbon tape and then coated with carbon by conventional resistive deposition. The employed accelerating voltage were 20 kV and currents ca. 3 × 10<sup>-8</sup> A for EPMA and ca. 1 × 10<sup>-10</sup> A for SEM, respectively.

## 2.4. Polymerization reactions

Polymerizations were performed using 0.25 dm<sup>3</sup> of toluene in a 1.00 dm<sup>3</sup> 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<sup>-5</sup> mol l<sup>-1</sup> of Zr was suspended in 0.01 dm<sup>3</sup> of toluene and transferred into the reactor under argon. The polymerizations were performed under atmospheric pressure of ethylene at 60 °C 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 60 °C for 4 h.

### 2.5. Polyethylene characterization

Molar masses and molar mass distributions were measured with a Waters CV plus 150 °C high-temperature GPC instrument, equipped with viscometrical detector, and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limit 1 × 10<sup>7</sup> for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1 cm<sup>3</sup> min<sup>-1</sup>. The analyses were performed at 140 °C. 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 ( $\chi_c$ ) were determined on using differential scanning calorimeter (Polymer Laboratories DSC) calibrated with Indium, at a heating and cooling rate of  $10^\circ\text{C min}^{-1}$  in the temperature range of  $30\text{--}150^\circ\text{C}$ . 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

At moderate activation temperatures, silica surface is mainly composed of isolated, and to a lesser extent, vicinal and geminal hydroxyl groups, as well as siloxane bridges. Lewis acid or base sites are absent unless it has been activated at very high temperatures, and Brønsted acidity is low or non-existent [11]. Silanol groups are capable to react with sequestering agents such as organometallic chlorides, hydrides and alkoxydes through the elimination of one or more of the original ligands [12]. In the present case, the reaction might

take place between PMHS Si–H groups and silica silanol groups. Preliminary experiments using PMHS content as far as 8.0 wt.% Si/SiO<sub>2</sub> showed that even under such conditions there are still isolated silanol groups available. The employed PMHS content (up to 3.0 wt.% Si/SiO<sub>2</sub>) should be far from silica surface saturation levels for such compound, guaranteeing accessible OH groups for subsequent metallocene grafting. Thus, zirconocene can potentially react by elimination of the chloride ligand with hydrogen atoms from silanol groups on the support, as well as with hydrogen atoms from PMHS chains. Therefore, we expect to generate two different catalyst centers one bound directly to silica surface and other to the PMHS chain.

Fig. 1 shows the dependence of zirconocene loading onto silica and catalyst system activity in ethylene homopolymerization on PMHS modifier concentration. As expected, grafting ( $n\text{BuCp}$ )<sub>2</sub>ZrCl<sub>2</sub> directly onto silica born the highest metal content (0.85 wt.% Zr/SiO<sub>2</sub>). Zirconocene graftings on modified silicas showed an abrupt reduction on Zr content with increasing amount of immobilized PMHS. For the support modified with 0.15 wt.% Si/SiO<sub>2</sub>, a reduction

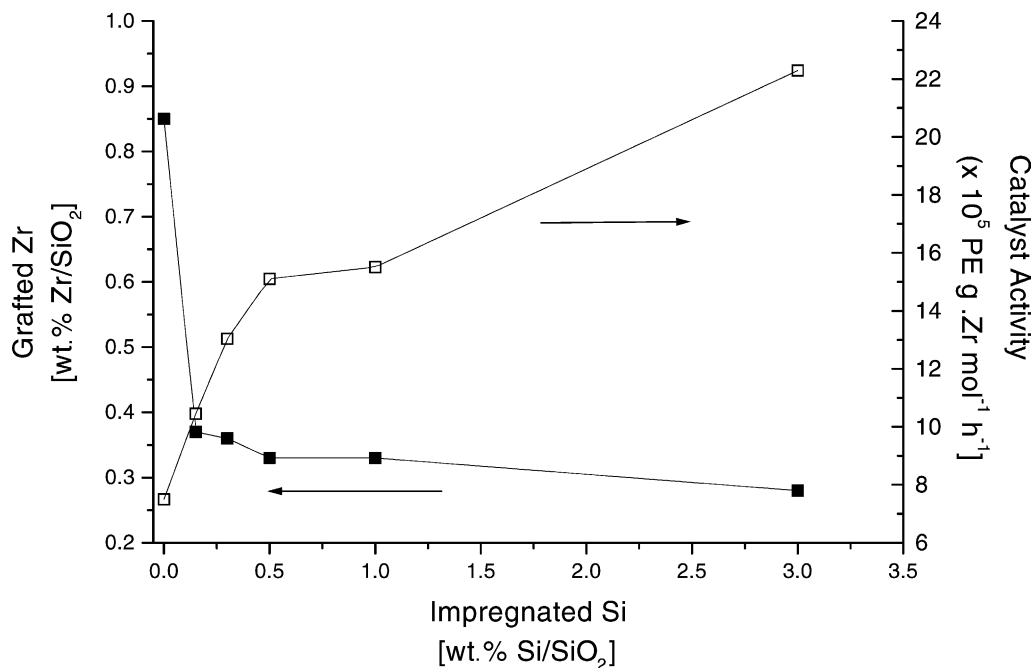


Fig. 1. Zr loading on silica from 1.5 wt.% Zr/SiO<sub>2</sub> solution of ( $n\text{BuCp}$ )<sub>2</sub>ZrCl<sub>2</sub> (■) and catalyst system activity in ethylene polymerization with MAO as co-catalyst (□) as a function of PMHS modifier concentration.

Table 1

The  $(n\text{BuCp})_2\text{ZrCl}_2$  loading on silica and catalyst activity in ethylene homopolymerization for different organosilicon modifiers (0.3 wt.% Si/SiO<sub>2</sub>)

| Organosilicon                      | Zirconocene loading (wt.% Zr/SiO <sub>2</sub> ) | Catalyst activity (10 <sup>5</sup> g PE (mol Zr h) <sup>-1</sup> ) |
|------------------------------------|---|--|
| (Bare SiO <sub>2</sub> )           | 0.85  | 7.5  |
| PMHS                               | 0.36  | 13.2   |
| Ph <sub>3</sub> SiCl <sup>a</sup>  | 0.50  | 15.0   |
| Me <sub>3</sub> SiCl <sup>a</sup>  | 0.60  | 18.9   |
| Me <sub>2</sub> SiHCl <sup>a</sup> | 0.12  | 11.4   |
| (Homogeneous)                      | –   | 12.3   |

Data for directly and unsupported metallocene are included for comparison. Polymerization conditions are as follows:  $P = 1$  atm;  $[\text{Zr}] = 10^{-5}$  mol l<sup>-1</sup> (toluene);  $[\text{Al}]/[\text{Zr}] = 2000$ ;  $T = 60$  °C; reaction time = 30 min.

<sup>a</sup> From [7].

of roughly 55% in grafted zirconocene is observed as compared with the case of bare silica. These results show that the consumption of silanol groups by organosilicon impregnation might impinge some steric effect on the residual ones, specially the open-silanol ones, influencing, therefore, in the amount of grafted zirconocene. Similar results were observed previously for other organosilicon modifiers following this abrupt reduction in the Zr grafted amount its content reduced slightly (from 0.37 to 0.27 wt.%) with PMHS impregnation [7]. Table 1 reports the final Zr grafted content on silica modified with various organosilicon compounds at 0.3 wt.% Si/SiO<sub>2</sub>, as well as catalyst activity in ethylene polymerization. According to Table 1, comparing Zr loadings on silica for samples treated with various organosilicon compounds, one infers that the ligands around the Si atom do influence the grafted metal content by the steric hindrance. Comparing, for instance, Ph<sub>3</sub>SiCl and Me<sub>3</sub>SiCl, the less sterically demanding Me<sub>3</sub> affords about 20% higher Zr loading as compared to Ph<sub>3</sub>. In the case of PMHS, an organosilicon polymer, which might be grafted at different silanol sites, the effect is much more significant in comparison to Ph<sub>3</sub>SiCl and Me<sub>3</sub>SiCl. It is worth mentioning that the very low Zr content observed in the case of Me<sub>2</sub>SiHCl was attributed to surface reaction between Si–H groups with  $(n\text{BuCp})_2\text{ZrCl}_2$ , leading to unstable catalyst species, which did not remain chemically bonded to the silica surface [7].

Also according to Fig. 1, despite the slight reduction in Zr grafted amount, catalyst activity monotonically

increased with increasing modifier concentration in the tested PMHS concentration range. The bimolecular catalyst deactivation process is a well-known factor in ethylene and propylene polymerization by zirconocenes [13–15]. Fischer and Mulhaupt [14] and Fischer et al. [15] proposed the formation of zirconocene dimers (i.e. electron deficient bridging complexes of two Zr centers) to account for the decay of the polymerization rate. Stehling et al. [16] suggested that the steric effect played by ligands would tend to prevent such deactivation. Grafting  $(n\text{BuCp})_2\text{ZrCl}_2$  on the PMHS-modified silica seems to generate more space among catalyst species on the surface, which guarantee a higher stability against the bimolecular deactivation by making the mutual approach of Zr centers sterically unfavorable.

Similar results were observed in the case of various organosilicon-modified silica (Table 1), and the increase in catalyst activity was similarly attributed to generation of more spaced zirconocene species [7]. It is worthy noting that, in the case of PMHS-modified silica, catalyst activity was shown to be even roughly higher than that observed in the case of homogeneous systems.

The modification of the support was evaluated by XPS. A typical XPS core-level spectrum of the Si 2p region is as shown in Fig. 2. The spectrum is characterized by an intense signal centered at ca. 103.3 eV attributed to Si from bulk SiO<sub>2</sub>. We also detected the presence of another species of Si, presenting lower binding energy (BE). This species can be attributed to PMHS, whose Si is located at the uttermost silica surface presenting, therefore, lower binding energy (BE).

The stepwise preparation of catalyst systems was further monitored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Fig. 3a presents the spectrum of silica surface activated under vacuum at 450 °C. The sharp peak at 3746 cm<sup>-1</sup> can be assigned to isolated, non-interacting silanol groups, while the very broad band placed at lower wavenumbers is due to hydrogen bonded pairs or chains of silanol [17,18].

The reaction of PMHS with silica surface imply consumption of hydrogen from silanol groups. Due to its structure, it is very likely that each polymeric unit might react with more than one OH group. Fig. 3b shows the DRIFTS spectrum of silica after reaction with PMHS in the amount of 0.3 wt.% Si/SiO<sub>2</sub>. The

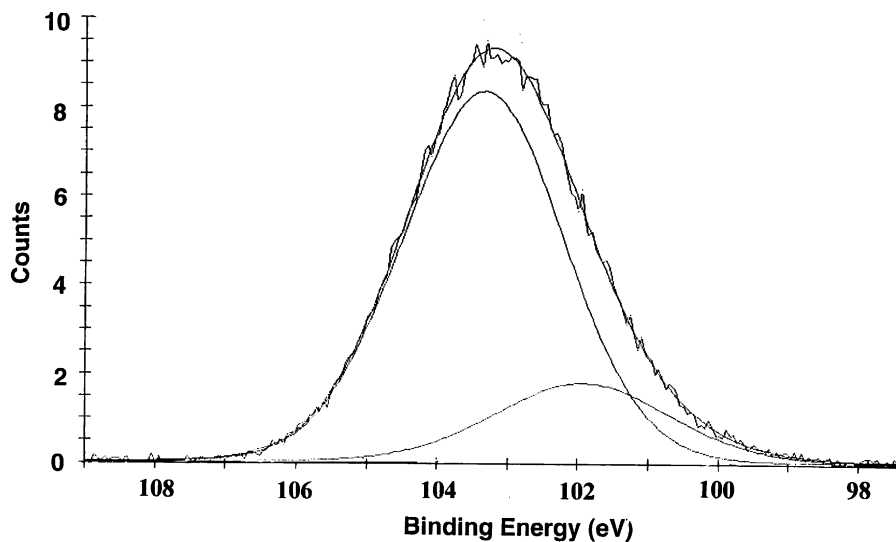


Fig. 2. Si 2p region spectrum of  $(n\text{BuCp})_2\text{ZrCl}_2$  supported on PMHS-modified silica having 0.30 wt.% Si/SiO<sub>2</sub>, together with its fitting components and their sum.

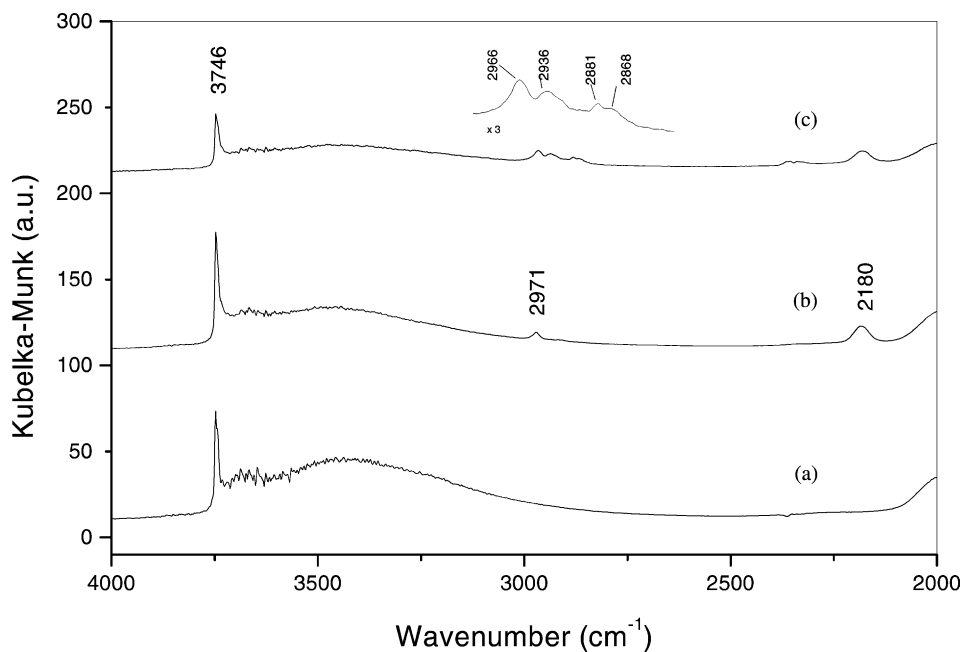


Fig. 3. DRIFTS spectra of: (a) SiO<sub>2</sub> dehydroxylated at 450 °C for 16h under vacuum; (b) same as in (a) followed by impregnation with 0.3 wt.% Si/SiO<sub>2</sub> toluene solution of PMHS; (c) same as in (b) followed by grafting a 1.5 wt.% Zr/SiO<sub>2</sub> toluene solution of  $(n\text{BuCp})_2\text{ZrCl}_2$  (resulting Zr content: 0.36 wt.% Zr/SiO<sub>2</sub>). In the inset, the region 3000–2800 cm<sup>-1</sup> is magnified with its intensity being multiplied by a factor of 3.



band placed at  $2971\text{ cm}^{-1}$  can be assigned to  $\text{CH}_3$  groups of the organosilicon polymer, while that at  $2180\text{ cm}^{-1}$  to  $\nu_{(\text{Si-H})}$  stretching band.

Following the silica modification with PMHS, the grafting with  $(n\text{BuCp})_2\text{ZrCl}_2$  led to the reduction of both isolated silanol ( $3746\text{ cm}^{-1}$ ) and Si-H groups ( $2180\text{ cm}^{-1}$ ), suggesting that the grafting might take place by the reaction with both the groups. In the case of the grafting  $(n\text{BuCp})_2\text{ZrCl}_2$  on 0.3 wt.% Si/SiO<sub>2</sub> PMHS-modified silica (see Fig. 2) we observed a reduction of 50 and 25% of the previous isolated silanol and the Si-H band intensity, respectively, which suggested that zirconocene seems to be more prone to react with the silanol groups than with the Si-H groups. In a similar monitoring experiment, in the case of 1.0 wt.% Si/SiO<sub>2</sub> PMHS-modified silica, the reduction of those band intensities were shown to be 37 and 10%, respectively. These values are coherent with the lower grafted metal content observed with the increase in PMHS content.

Also in Fig. 3, four new bands appeared (see inset), corresponding to the asymmetric and the symmetric  $\nu_{(\text{C-H})}$  stretching bands in the  $\text{CH}_3$  and  $\text{CH}_2$  fragments of the  $n\text{Bu}$  groups. These wavenumbers bands practically agree with those observed when  $(n\text{BuCp})_2\text{ZrCl}_2$  was grafted directly onto silica [19].

Concerning the persistence of the isolated silanol  $\nu_{(\text{O-H})}$  stretching band at  $3746\text{ cm}^{-1}$  even after zirconocene impregnation, it is worthy mentioning that previous FT-IR monitoring of the grafting of  $(n\text{BuCp})_2\text{ZrCl}_2$  at the surface of the activated silica in loadings close to the saturation have shown that the major part of OH groups is not consumed [19]. This was attributed to the presence of bulky ligands in the catalyst molecule, which seems to prevent the remaining OH groups from the reaction [19]. Similar results were also observed in the case of organosilicon compounds, such as  $\text{Ph}_3\text{SiCl}$  and  $\text{Me}_2\text{SiHCl}$  [7].

The catalyst surface composition was also probed by XPS. Table 2 reports the Zr content for the various resulting supported systems. For comparative reasons the data from RBS measurements were also included. The catalyst grafting takes place preferentially at the external surface of the silica grains. Comparing the metal contents determined by RBS and XPS, we observe that the metal contents from the RBS measurements are systematically lower than those obtained by XPS. In the case of RBS, assuming that silica is in

Table 2

Zr loading on PMHS-modified silicas determined by RBS and XPS and Zr 3d<sup>5/2</sup> binding energy and signal energy width of the various supported systems

| Si/SiO <sub>2</sub><br>(%) | Zr/SiO <sub>2</sub><br>(RBS; %) | Zr/SiO <sub>2</sub><br>(XPS; %) | BE<br>(eV)     | FWHM <sup>a</sup><br>(eV) |
|----------------------------|---------------------------------|---------------------------------|----------------|---------------------------|
| 0.00                       | 0.85                            | 1.20                            | 182.4          | 2.5                       |
| 0.15                       | 0.37                            | 0.81                            | 182.0<br>183.7 | 1.9<br>1.9                |
| 0.30                       | 0.36                            | 0.80                            | 181.5<br>183.3 | 2.2<br>2.7                |
| 0.50                       | 0.33                            | 0.59                            | 182.6          | 2.6                       |
| 1.00                       | 0.33                            | 0.51                            | 182.9          | 2.7                       |
| 3.00                       | 0.28                            | 0.44                            | 183.0          | 2.7                       |

<sup>a</sup> FWHM: full width at half maximum intensity.

its crystalline form ( $\alpha$ -quartz), the reach of 2.0 MeV He<sup>+</sup> 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 sensitive to the outermost surface composition, where the relative contribution of Zr atoms is much more important. In spite of the numeric differences between both techniques, the grafted metal content evidenced the same trend among the various supported catalysts.

In the XPS analysis, varying the angle between the surface and the detector can yield a metal depth profile in the samples. Fig. 4 shows Zr/SiO<sub>2</sub> content at different takeoff angles for sample bearing 3.0 wt.% Si/SiO<sub>2</sub>. According to it, the highest Zr/SiO<sub>2</sub> content is observed at  $\alpha = 45^\circ$  (more surface glancing) indicating that zirconium grafted layer is preferentially on the outermost surface of the catalyst substrate, corroborating the earlier discussion.

Table 2 includes also the binding energies (BE) of the zirconocene surface species generated on the various supported systems. The XPS core level spectrum of Zr is characterized by two signals due to the spin-orbital coupling of its 3d electrons one at ca. 183.0 eV (3d<sup>5/2</sup>) and the other at ca. 185.0 eV (3d<sup>3/2</sup>), bearing always a split of 2 MeV [6,20]. For the sake of simplicity, we present in Table 2 data concerning only the 3d<sup>5/2</sup> signals. Neat  $(n\text{BuCp})_2\text{ZrCl}_2$  presents a 3d<sup>5/2</sup> signal at 181.6 eV, which is shifted to 182.4 eV when supported onto silica. The shift to

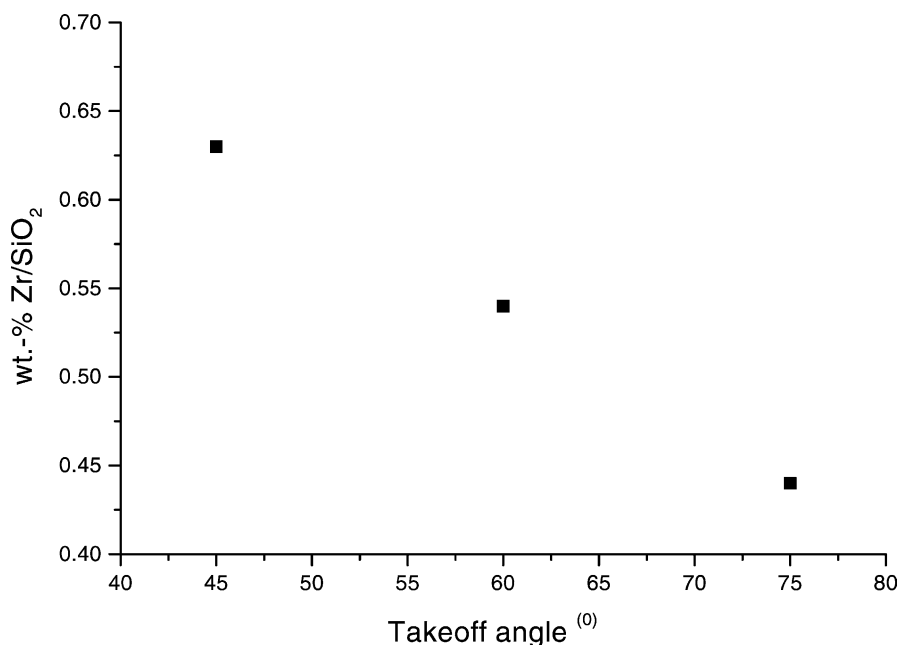


Fig. 4. Relationship between the probed Zr/SiO<sub>2</sub> ratio and the takeoff angle for a sample of (*n*BuCp)<sub>2</sub>ZrCl<sub>2</sub> supported on PMHS-modified silica having 3.00 wt.% Si/SiO<sub>2</sub>.

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. The immobilization of low organosilicon contents (up to 4.0 wt.%) on the PMHS-modified silica generated two zirconocene species: one with lower BE (corresponding to an area of ca. 30%) and another with higher BE (in majority). The presence of two species can be due to a large availability of silanol groups which were not consumed by the silica reaction with PMHS.

According to Table 2, considering the catalysts systems bearing only one surface species, the BE of the resulting zirconocenes species increases with the amount of PMHS on the surface increases, which means that such species are more electron deficient in comparison to those, for instance, generated on the bare silica support. The increase in catalyst activity with the reduction in the BE of Zr was reported in the literature for both homogeneous [21] and supported catalysts [6,20]. In the present study, a contrary phenomenon is observed, i.e. catalyst activity increases as the grafted metal content is reduced and as the BE of the resulting zirconocenes species increases. Both electronic and

steric effects can impinge influence on catalyst activity. In order to evaluate solely the electronic influence of PMHS in the catalyst system, we performed some homogeneous polymerization, adding the organosilicon in different zirconocene/PHMS ratios (Fig. 5).

According to Fig. 5, addition of PMHS to the reaction milieu reduces roughly 50% of the catalyst activity in comparison to that observed in the absence of PMHS. Thus, although we cannot assume that the effect of PMHS in the homogeneous systems might be necessarily the same as that in supported ones, it seems that the increase in the catalyst activity observed in the supported systems based on PMHS-modified silica should be attributed to steric effect related to the generation of more spaced species which would hinder the bimolecular deactivation reactions.

The full width at half maximum intensity (FWHM) of XPS signals can traduce the heterogeneity in the nature of the zirconocene species. Nevertheless, we can observe in Table 2 that there is not a significant difference among the various supported systems bearing only one surface species.

The morphology of the resulting catalysts was observed by scanning electron microscopy (SEM).



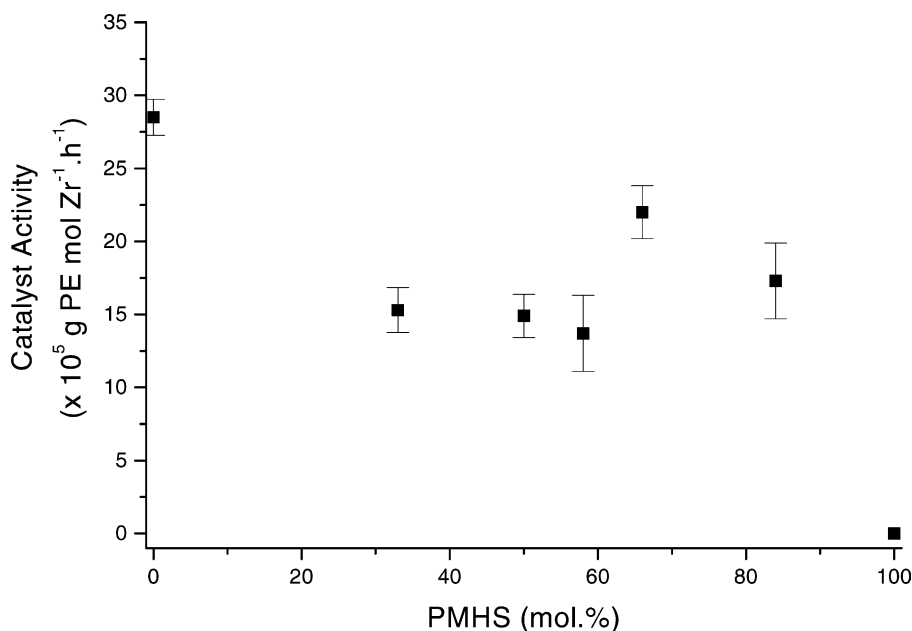


Fig. 5. Catalyst activity in homogeneous ethylene polymerization with MAO as co-catalyst as function of PMHS concentration.

According to Fig. 6 (left) the original support morphology was kept in the resulting catalysts, maintaining the spherical shape. The spatial distribution of the zirconocene was evaluated by EPMA, by detecting the Zr characteristic X-ray emission. The resulting Zr distribution maps in the catalyst particle are shown in Fig. 6 (right). Low metal content corresponds to the darker region, while higher metal content to the brighter one. According to Fig. 6, the Zr content is roughly uniformly distributed on the surface of the particle both in the silica modified with 0.15 and 3.00% Si/SiO<sub>2</sub>.

Concerning the polymer characterization, all the catalyst systems produced polyethylene with practically constant melting and crystallization temperatures at  $135 \pm 0.6$  and  $119 \pm 0.7$  °C, respectively. These temperatures are typical of linear high-density polyethylenes. Table 3 presents weight average molecular weight ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) of the polyethylenes produced with the various support systems. Excepting polymers produced with zirconocene supported on bare silica,  $M_w$  was shown to be reduced as the amount of PMHS increases. A possibility for such behavior is that the excess amount of PMHS resulted in an increase of non-bound region of

Table 3  
Properties of polyethylenes produced using different (*n*BuCp)<sub>2</sub>-ZrCl<sub>2</sub> supported catalysts

| PMHS treatment (wt.% Si/SiO <sub>2</sub> ) | $M_w$ ( $10^{-5} \text{ g mol}^{-1}$ ) | $M_w/M_n$ |
|--|--|-----------|
| –  | 2.3                                    | 2.4       |
| 0.15                                       | 4.7                                    | 2.0       |
| 0.30                                       | 3.0                                    | 2.5       |
| 0.50                                       | 1.9                                    | 2.1       |
| 1.0  | 1.7                                    | 1.8       |
| 3.0  | 1.3                                    | 2.6       |

PMHS chains. Zr species bound on such region could be protected from  $\beta$ -transfer and deactivation, but not from chain-transfer to Al-species. Such effects could explain the decreased  $M_w$  obtained with high-PMHS supports.

Table 4 presents data concerning  $M_w$  and  $M_w/M_n$  of the polymers produced with some homogeneous systems.  $M_w$  remained in the range of  $(1.1\text{--}1.6) \times 10^5 \text{ g mol}^{-1}$ . Higher  $M_w$  were observed in the case of 66 PMHS (wt.% mol), probably due to the highest activity exhibited by this system. No clear trend could be observed in terms of the polydispersity index for the polymers both produced by homogeneous and

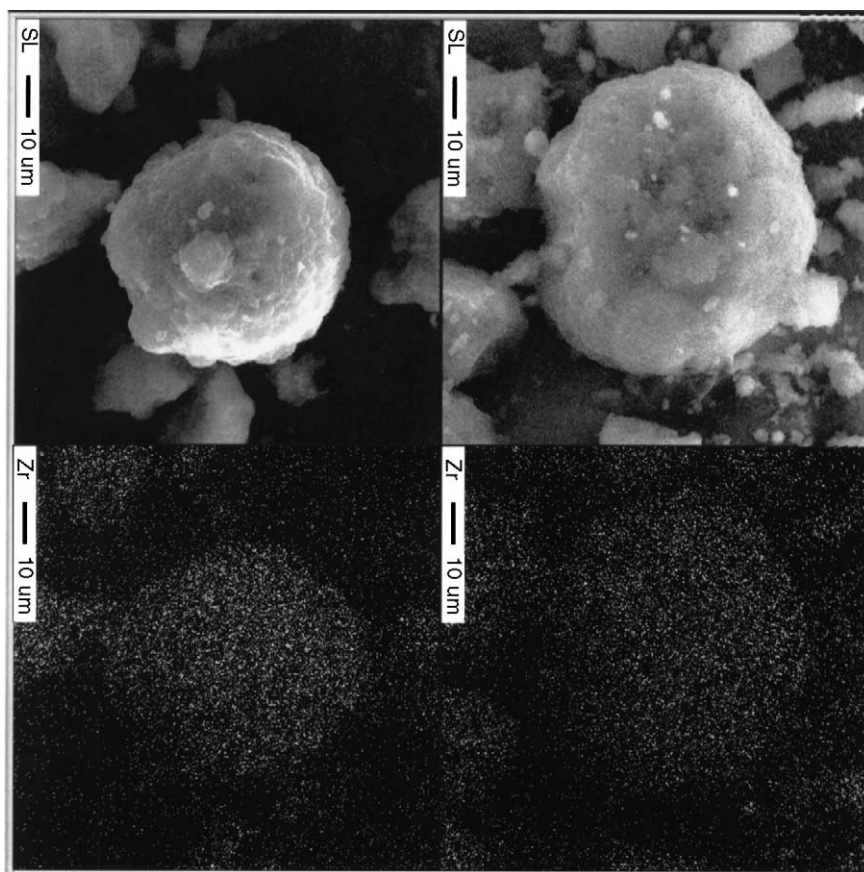


Fig. 6. Top: 3.00 wt.% Si/SiO<sub>2</sub> support; bottom: 0.15 wt.% Si/SiO<sub>2</sub>; left: SEM micrograph of the resulting catalysts; right: Zr distribution map in the resulting catalyst.

supported systems. Comparing  $M_w$  data from Tables 3 and 4, polyethylenes produced with the supported systems presented higher molecular weight than those obtained with the soluble systems. Similar behavior has already been observed [22] and attributed to the block-

ing of the polymerization active sites by the support of hindering the deactivation step and the  $\beta$ -elimination transfer. In other words,  $\beta$ -elimination transfer between two metallocene centers is hindered, resulting in a larger growth of the polymer chain and, so in higher molecular weight [23].

Table 4

Properties of polyethylenes produced by homogeneous (*n*BuCp)<sub>2</sub>-ZrCl<sub>2</sub> in the presence of different amounts of PMHS

| PMHS (mol%) | $M_w \times 10^{-5} \text{ g mol}^{-1}$ | $M_w/M_n$ |
|-------------|---|-----------|
| –           | 1.6                                     | 2.5       |
| 33.3        | 1.1                                     | 2.6       |
| 50.0        | 1.4                                     | 3.3       |
| 58.0        | 1.4                                     | 2.2       |
| 66.6        | 4.0                                     | 2.8       |

#### 4. Conclusions

The chemical modification of the silica with PMHS prior to the zirconocene grafting seems to be a potential approach to keep apart metallocene species on the silica surface, and this approach increases the catalyst activity by preventing the deactivation reaction. The amount of grafted zirconocene is reduced with the

organosilicon content on silica. DRIFTS monitoring showed that most of the isolated silanol groups on the silica support are not consumed by the modification with an amount of PMHS given the range of PMHS content in this study. Subsequent zirconocene grafting did not lead to a total consumption of the residual OH groups, and it is probably due to the steric hindrance played by the bulky *n*BuCp ligands. Part of Si–H groups of the organosilicon polymer groups are also consumed during the zirconocene grafting.

The addition of PMHS to the polymerization medium in the homogeneous systems reduces the catalyst activity. The spacers in a suitable concentration among the metallocenes species can increase the catalyst polymerization activity. Earlier mentioned observation supports the evidence that the support modification stabilizes the surface metallocene species and prevents the bimolecular deactivation reaction.

The spatial distribution of Zr species on the silica surface was shown by EPMA to be homogeneous, while angle resolved XPS showed its depth distribution of Zr to be mainly at the outer surface.

Concerning the polymer properties, the low concentration PMHS-modified supported catalysts produced the polymers with higher  $M_w$  which indicate higher stability of the polymerization active species as compared with the one in the homogeneous systems.

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