

Organosilicon-modified silicas as support for zirconocene catalyst

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Abstract

The metallocene ($n\text{BuCp}$)₂ZrCl₂ was grafted on partially dehydroxylated commercial silica (Grace 948) whose surface had been chemically modified by wet impregnation of an organosilane (Ph₃SiCl, Me₃SiCl, or Me₂SiHCl) aiming at supported catalyst systems with well spaced α -olefin polymerization active centers. Final Zr loadings were determined by Rutherford Backscattering Spectrometry (RBS), and modifications at the silica surface after each preparation step were monitored by in situ FT-IR spectroscopy. These catalyst systems produced polyethylenes with narrow molecular weight distribution when methylaluminoxane was used as cocatalyst, with twice the activity of ($n\text{BuCp}$)₂ZrCl₂ supported on bare SiO₂. Effects of support structure and chemical modification on catalyst performance are presented and discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metallocene catalysts are becoming increasingly important in α -olefin polymerization. Metallocene/methylaluminoxane (MAO) systems combine high activity with the possibility of tailoring polymer properties [1–4]. Depending on ligand geometry, these catalysts permit strong control of homopolymer regio- and stere-

oregularity and molecular weight distribution, as well as copolymer synthesis with uniform comonomer distribution. Moreover, polymer properties such as temperature resistance, hardness, impact strength, and transparency can be precisely controlled through the metallocene structure. About 2% of the world's polyethylene (PE) production is already based on metallocene catalysts and it is believed that within 10 years this quota will reach 20% [5]. The rapid market penetration of metallocene-based PE is due to high-value attributes such as greater stiffness and impact strength, greater stretch and puncture resistance, and improved sealability as

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compared to PEs produced by conventional Ziegler–Natta catalysts.

Unfortunately, metallocenes require large amounts of expensive MAO to yield maximum catalyst activity. This, to some extent, may impair their commercial application. Therefore, much effort has been made not only to lower the amount of MAO in polymerization but also to find a new cocatalyst to replace it. Satisfactory results have been obtained, for instance, using organoboron activators [6–8]. In this case, a significant advantage is that only a stoichiometric amount of the cocatalyst is required to achieve maximum activity.

Besides the demand of MAO in high amounts, soluble metallocene catalysts present other disadvantages. A solution polymerization process requires separation of the polymer and removal, recovery, and purification of the solvent. On the other hand, gas phase processes have lower cost and energy consumption. As most of the existing polymerization plants run slurry- and gas-phase processes with heterogeneous catalyst systems, homogeneous catalysts must be heterogenized if rapid application is aimed. Moreover, metallocene heterogenization is desirable to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive polymer swelling, and to produce polymer particles of a desired regular morphology.

Several silica-supported metallocene catalyst systems have been reported [9,10]. They may be grouped into two types: MAO mediated [11–13] (in which the surface of silica is modified with MAO prior to metallocene impregnation) and directly supported [14–16]. These procedures afford different catalysts, which, in turn, produce polyolefins with different properties. In several cases, it is claimed that additional MAO is not necessary during polymerization if it is initially immobilized on the silica surface. Besides MAO, a borate cocatalyst has also been proposed to modify silica prior to zirconocene grafting [17]. Very recently, cuboctametric silsesquioxane mono(silanol), which is employed to mimic the surface of partially dehy-

droxilated silica, was used in modeling the surface reaction between metallocenes and silica [18].

So far, metallocene heterogenization studies indicate that physical impregnation onto or grinding with supports such as silica does not give rise to a catalyst system of practical application. This is due to a drastic reduction of catalyst activity, mainly attributed to the rather low quantities of metallocene immobilized [19–21]. Another reason might be the presence of the silica surface itself, which plays the role of a sterically demanding ligand close to the active site, therefore inhibiting monomer coordination. Finally, catalyst systems with higher metal contents achieved by chemical impregnation suffer destruction of active sites from bimetallic interaction.

Most of the studies employing chemically-modified silicas concern improving monomer access to active sites through the use of a spacer between the silica surface and the metallocene species, and, as judged from reported catalyst activities, many have been quite successful. Silanes with cyclopentadienyl groups directly bonded to the silicon atom have been used for immobilizing metallocene complexes on silica [22]. Catalyst systems in which CpIndZrCl_2 was anchored on silicas modified with trisiloxane or pentamethylene spacers were shown to be more active than those prepared by direct impregnation [23]. Soga et al. [24] prepared some supported catalysts in which silica was initially modified with Cl_2SiMe_2 , followed by MAO, prior to Cp_2ZrCl_2 grafting. Such systems were shown to be active in the presence of common trialkylaluminum cocatalysts. The immobilization of Cp_2ZrMe_2 on silica chemically modified with Me_3SiCl was claimed to yield a catalyst system of fairly high activity in ethylene polymerization even in the absence of any cocatalyst [25]. Very recently, PhSiH_3 was used to modify the silica surface prior to hydroxy-modified borate immobilization, generating a heterogeneous borate cocatalyst [26]. The issue of bimetallic deactivation, by its turn, has been addressed in

the development of chromocene catalysts used in ethylene polymerization. Compounds such as hexamethyldisilazane were used as silica-modifying agents aimed at generating catalyst species more spaced among themselves, thus avoiding eventual bimolecular interactions [27].

In the following, we describe supported catalyst systems prepared by grafting of $(n\text{BuCp})_2\text{ZrCl}_2$ either onto partially dehydroxilated or additionally organosilicon-modified silica Grace 948. Metal loadings were determined by Rutherford Backscattering Spectrometry (RBS), and surface reactions were monitored by transmission Infrared Spectroscopy (FT-IR). The catalyst systems were tested in ethylene homopolymerization using MAO as cocatalyst. Effects of the nature of the organosilicon modifier as well as of its content on silica were evaluated on catalyst activity and on polymer properties (molecular weight, crystallinity, polydispersity, and melting [T_m] and crystallization [T_c] temperatures). For comparative reasons, the homogeneous system was equally tested.

2. Experimental

2.1. Materials (chemicals)

Silica Grace 948 ($255 \text{ m}^2 \text{ g}^{-1}$) was activated under vacuum ($P < 10^{-4}$ mbar) for 16 h at 723 K. The support was then cooled to room temperature under dynamic vacuum and stored under dried argon. MAO (gently supplied by Witco, 10.0 wt.% toluene solution, average molar mass 900 g mol^{-1}), $(n\text{BuCp})_2\text{ZrCl}_2$ (Witco), Ph_3SiCl (Aldrich), Me_3SiCl (Aldrich), and Me_2SiHCl (Merck) 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. Pure grade toluene and methyl dichloride 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. Organosilicon-modified silicas were prepared by impregnating 1.0 g of activated silica with a toluene solution of organosilicon corresponding to 0.15–1.00 wt.% Si/SiO₂, stirred at room temperature for 30 min. The solvent was removed under vacuum, a toluene solution of $(n\text{BuCp})_2\text{ZrCl}_2$ corresponding to 1.5 wt.% Zr/SiO₂ was added, 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 $12 \times 2.0 \text{ cm}^3$ of toluene and dried under vacuum for 4 h. An analogous procedure was employed for supporting the catalyst onto bare SiO₂, but in this case the organosilicon impregnation step was suppressed. Such methods have shown to afford stable supported metallocene systems [28].

2.3. RBS

Zirconium loadings on silica 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 particles elastically scattered in the Coulombic field of the atomic nuclei in the target [29]. In this study, the Zr/Si atomic ratio was determined from the relative intensities 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 [29,30].

2.4. Fourier-transform infrared spectroscopy

Transmission FT-IR spectra were recorded on a Bomem MB-102 Spectrometer, (32 scans at a 4 cm^{-1} resolution). The study was re-

stricted to the mid-infrared region (3800–2000 cm^{-1}) due to strong bulk absorption of silica at lower wavenumbers. The samples consisted of 25–35 mg of silica Aerosil pressed under 12 MPa into self-supporting tablets ($\varnothing = 17$ mm) which were introduced into a Pyrex cell with CaF_2 windows. The unit was attached to a greaseless glass gas/vacuum handling system and the silica tablet in situ activated under vacuum ($< 10^{-4}$ mbar) at 723 K for 16 h. The infrared spectroscopic study was carried out using Aerosil (pyrogenic silica) because such silicas are non-porous, have a very low bulk density, and can easily be compacted into transparent self-supporting discs for transmission studies. Their spectral properties do not differ greatly from those of precipitated silicas or silica gels (like the silica Grace, employed in this work), except that the latter can have a greater diversity of micro- and mesoporosity and some types are quite granular and difficult to press into transparent discs [31].

Impregnations were sequentially conducted from methyl dichloride solutions containing organosilicon, with amounts equivalent to those employed in the chemical modification of silica Grace, and $(n\text{BuCp})_2\text{ZrCl}_2$, with amounts corresponding to those determined by RBS for the aforementioned catalyst systems. Methyl dichloride was employed instead of toluene because it is more easily removed under vacuum in the drying step. All spectra were recorded at room temperature.

2.5. Polymerization reactions

Ethylene homopolymerizations were performed in 0.25 dm^3 of toluene in a 1.00 dm^3 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/Zr molar ratio of 2000. In each experiment, a mass of catalyst system corresponding to 10^{-5} mol l^{-1} of Zr was suspended in 0.01 dm^3 of toluene and transferred into the reactor under

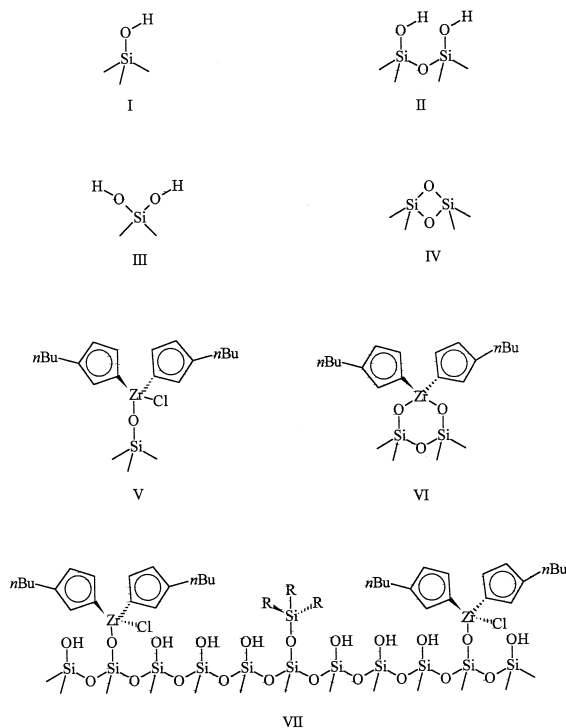
argon. Polymerizations were performed at atmospheric pressure of ethylene, at 333 K, for 30 min. Acidified (HCl) ethanol was used to quench the processes, and reaction products were separated by filtration, washed with distilled water, and, finally, dried under reduced pressure at 333 K. Each polymerization reaction was repeated at least three times under identical conditions, leading to similar products.

2.6. 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, since the former is influenced by the mechanical and thermal history of the samples. Molar masses and molar mass distributions were investigated with a Waters CV plus 150 C high-temperature GPC instrument, equipped with viscometrical detector, differential optical refractometer, and three Styragel HT type columns (HT3, HT4, and HT6) with exclusion limit 1×10^7 for polystyrene. 1,2,4-trichlorobenzene was used as solvent, at a flow rate of 1 $\text{cm}^3 \text{min}^{-1}$. All analyses were performed at 413 K. The columns were calibrated with standard polystyrenes of narrow molar mass distribution and with linear low-density polyethylenes and polypropylenes.

3. Results and discussion

Silica is one of the simplest oxides because its surface, at least for moderate activation temperatures, is mainly composed of isolated (**I**) and, to a lesser extent, vicinal (**II**) and geminal (**III**) hydroxyl groups, as well as relatively unreactive siloxane bridges (**IV**) (Scheme 1). Lewis acid/base sites are absent unless it has been activated at very high temperatures, and Brønsted acidity is low or non-existent [32].



Scheme 1.

The surface density of silanol groups on a fully hydroxylated silica has been found to be about 4.9 nm^{-2} , regardless of the type of silica, [33] but thermal treatment at 723 K reduces this number to about $1.2\text{--}1.5 \text{ nm}^{-2}$ by silanol condensation [34]. Silanol groups are capable to react sequestering agents such as organometallic chlorides and alkoxydes, with elimination of one or more of the original ligands. In the present case, metallocenes are grafted on the silica surface by elimination of the chloride ligand with hydrogen atoms from silanol groups on the support, generating mono- (V) or bidentate (VI) surface species, depending upon the surface density of OH groups.

Monodentate species are potentially active polymerization sites. Nevertheless, deactivation can occur through bimolecular reaction between neighboring centers, which should be avoidable by spacing such catalyst species (VII) on the silica surface. Spacing can be achieved by consuming a fraction of silanol groups prior to

metallocene grafting, so as to produce well-separated residual OH groups (immobilization sites). In this work, partially dehydroxylated silica Grace 948 was chemically modified with up to 1.0 wt.% Si/SiO₂ Ph₃Si- groups. Such concentrations are far from silica surface saturation levels for analogous and even larger organometallic compounds, [35] guaranteeing residual OH groups for metallocene grafting.

Fig. 1 shows the dependence of zirconocene loading onto silica and catalyst system activity in ethylene homopolymerization on Ph₃Si-modifier concentration. As expected, grafting (*n*BuCp)₂ZrCl₂ directly onto silica born the highest metal content (0.85 wt.% Zr/SiO₂). Zirconocene graftings on modified silicas showed a reduction on Zr content with increasing amount of organosilicon immobilized. For the support modified with 1.0 wt.% Si/SiO₂, a reduction of almost 60% in grafted zirconocene is observed as compared to the case of bare silica. These results show that the consumption of silanol groups by organosilicon impregnation allows tailoring of the amount of grafted zirconocene.

Catalyst activity was seen to increase with increasing modifier concentration up to 0.3 wt.% Si/SiO₂. The bimolecular catalyst deactivation process is a well-known factor in ethylene and propylene polymerization by zirconocenes [36–38]. Fischer et al. proposed zirconocene dimers (i.e., electron deficient bridging complexes of two Zr centers) to account for the decay of the polymerization rate [37,38]. Stehling et al. [39] suggested that bulky ligands would tend to thwart such deactivation. Grafting (*n*BuCp)₂ZrCl₂ on the organosilicon-modified silica seems to generate more spaced catalyst species on the surface, which in turn guarantee a higher stability against bimolecular deactivation by making the mutual approach of Zr centers sterically unfavorable.

Iiskola et al. [40] also observed an almost six-fold catalyst activity increase for CpZrCl₃ immobilized on a modified-silica surface as compared to CpZrCl₃ on bare SiO₂. In those

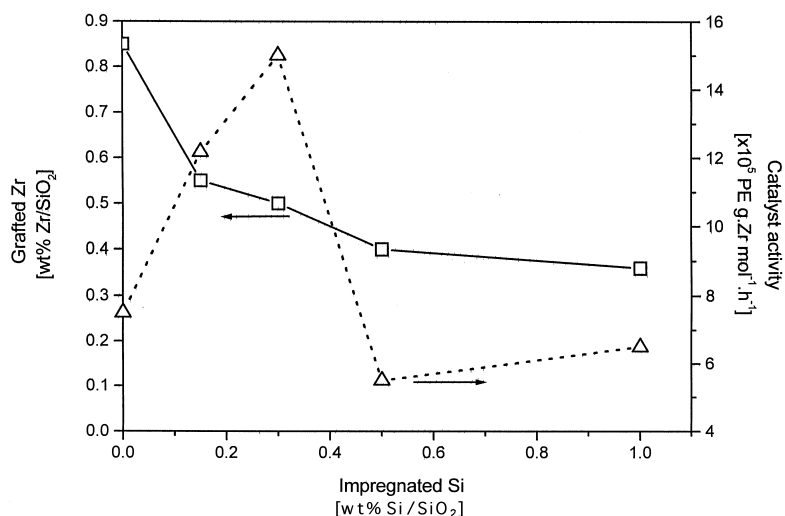


Fig. 1. Zr loading on silica from a 1.5 wt.% Zr/SiO₂ solution of (nBuCp)₂ZrCl₂ (□) and catalyst system activity in ethylene homopolymerization with MAO as cocatalyst (Δ) as a function of Ph₃SiCl modifier concentration.

systems, the support was previously modified with Cp-silicon alkoxyde, which rendered the active sites separated from the surface. The high catalyst activity was attributed to an activating effect of the Cp groups on the surface. Lee et al. [23] observed that the catalyst activity of CpIndZrCl₂ was four to five times higher when the metallocene was supported on trisiloxane- or pentamethylene-modified silica, when compared to the CpIndZrCl₂/SiO₂ system. In the present work, we observed that the catalyst activity tripled when silica was modified with 0.3 wt.% Si/SiO₂, comparing to (nBuCp)₂ZrCl₂/SiO₂.

Higher organosilicon amounts (0.5–1.0 wt.% Si/SiO₂) might render catalytically active sites even more spaced, as inferred from the resulting metal loadings in Fig. 1. Nevertheless, a drop in catalyst activity was observed for such organosilicon contents. It seems that the presence of Ph₃Si- groups in amounts higher than 0.3 wt.% Si/SiO₂ deactivates catalyst species. Further studies, employing also homogeneous metallocenes, are necessary to evaluate the activating/deactivating effect of the phenyl groups on (nBuCp)₂ZrCl₂.

The stepwise preparation of catalyst systems in this study was monitored by transmission

infrared spectroscopy. Fig. 2a presents the spectrum of a silica surface activated under vacuum at 723 K. The sharp peak at 3747 cm⁻¹ can be assigned to isolated, non-interacting silanol groups, while the very broad band centered about 3692 cm⁻¹ is due to hydrogen bonded pairs or chains of silanols [41,42].

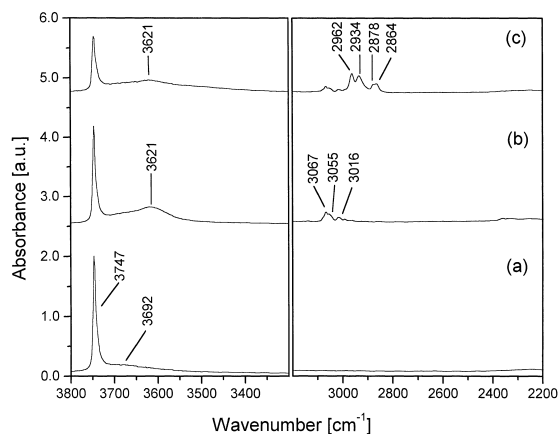


Fig. 2. IR spectra in the 3800–3300 cm⁻¹ and 3200–2200 cm⁻¹ regions of: (a) SiO₂ dehydroxylated at 723 K for 16 h under vacuum. (b) same as in (a) followed by impregnation at 298 K with a 1.0 wt.% Si/SiO₂ methylchloride solution of Ph₃SiCl; (c) same as in (b) followed by impregnation at 298 K with a 0.32 wt.% Zr/SiO₂ toluene solution of (nBuCp)₂ZrCl₂. The right hand side of the spectra is multiplied by a factor of 6.

Ph_3SiCl was used to chemically modify silica, presumably according to the following reaction:



IR evidence for this reaction comes from an observed intensity decrease for the isolated SiOH band at 3747 cm^{-1} . Modification at the 1.0 wt.% Si/SiO₂ level leads to a 16% intensity reduction, indicating that isolated OH groups were either consumed by the surface reaction or perturbed, since the appearance of a broad band centered at 3621 cm^{-1} is also observed (Fig. 2b).

The impregnation of Ph_3Si - groups is also accompanied by the appearance of three bands in the region of aromatic $\nu_{\text{O-H}}$, corresponding to the stretching vibration of the phenyl groups: 3067, 3055 and 3016 cm^{-1} . It is worth mentioning that aromatic $\nu_{\text{C-H}}$ appears as bands close to 3038 cm^{-1} , which can be explained in terms of a single fundamental absorption accompanied by a series of weaker absorptions arising from combinations of the various bands in the $1600\text{--}1400 \text{ cm}^{-1}$ region [43]. In the $\nu_{\text{O-H}}$ region, a large band is now centered at 3621 cm^{-1} , which may result from an interaction between surface silanol and aromatic phenyl groups, in analogy with literature data attributing surface silanol $\nu_{\text{O-H}}$ bands at 3645 and 3510 cm^{-1} to vicinal OH groups interacting with aromatic groups through hydrogen bonding [44]. Similar results have also been reported concerning the adsorption of anisole onto surface silanol groups [45]; IR bands in the $3600\text{--}3400 \text{ cm}^{-1}$ region were attributed to surface species resulting from the interaction of hydrogen-containing groups with the π -electron system of the aromatic ring.

Following silica Aerosil modification with Ph_3SiCl , impregnation with $(n\text{BuCp})_2\text{ZrCl}_2$ at the 0.32 wt.% Zr/SiO₂ level (corresponding to the grafted metal loading determined by RBS on silica Grace 948 submitted to the same pretreatment) lead to further intensity reduction in the IR band associated to isolated silanol groups.

The bands corresponding to Ph_3Si - groups were not affected by the presence of the metallocene on the surface. Besides, four new bands appear between 2962 and 2864 cm^{-1} , corresponding to asymmetric and symmetric $\nu_{\text{C-H}}$ in the CH_3 and CH_2 fragments of the $n\text{Bu}$ groups. These wavenumbers practically coincide with those observed when $(n\text{BuCp})_2\text{ZrCl}_2$ was grafted directly onto silica [46]. Analogous results were observed by FT-IR when silica was modified with 0.30 wt.% Si/SiO₂ followed by 0.50 wt.% Zr/SiO₂.

Concerning the persistence of the isolated silanol $\nu_{\text{O-H}}$ band at 3747 cm^{-1} even after zirconocene impregnation, it is worth mentioning that FT-IR monitoring of the grafting of $(n\text{BuCp})_2\text{ZrCl}_2$ at the surface of activated silica in loadings close to saturation have shown that a major part of OH groups is not consumed. This is probably due to the presence of bulky ligands in the catalyst molecule, which seem to prevent the remaining OH groups from reacting [46].

Organosilicon compounds less sterically demanding than Ph_3SiCl were also tested as silica-modifying agents. Table 1 presents resulting zirconium loadings on silica, as well as catalyst system activities. For comparative reasons, data concerning $(n\text{BuCp})_2\text{ZrCl}_2$ in homogeneous milieu and Ph_3SiCl -modified silicas are also included.

In Table 1, comparing the homogeneous system to the one prepared by direct grafting of $(n\text{BuCp})_2\text{ZrCl}_2$ onto silica, one observes a significant drop in catalyst activity. Activity reduction due to catalyst immobilization has already been mentioned in literature [19–21,29]. It should be considered that, in the homogeneous systems, all metallocene molecules present in the milieu are potentially active centers. This is not likely in supported systems, in which a variety of surface species (not necessarily active) can be formed during the grafting process. Moreover, the silica surface itself plays the role of a sterically demanding ligand, which might in part render difficult the access of the monomer to the catalytic center.

Table 1

The $(n\text{BuCp})_2\text{ZrCl}_2$ loading on silica and catalyst activity in ethylene homopolymerization for different organosilicon modifiers at different concentrations. Data for directly supported and unsupported metallocene are included for comparison
 Polymerization conditions as follows: $P = 1$ atm; $[\text{Zr}] = 10^{-5}$ mol \cdot l $^{-1}$ (toluene); $[\text{Al}]/[\text{Zr}] = 2000$; $T = 333$ K; reaction time = 30 min.

Organosilicon	Modifier loading (wt.% Si/SiO ₂)	Zirconocene loading (wt.% Zr/SiO ₂)	Catalyst Activity (10 ⁵ g PE (mol Zr h) ⁻¹)
(Bare SiO ₂)	–	0.85	7.5
Ph ₃ SiCl	0.30	0.50	15.0
	1.00	0.32	6.5
Me ₃ SiCl	0.30	0.60	18.9
	1.00	0.38	12.0
Me ₂ SiHCl	0.30	0.12	11.4
(Homogeneous)	–	–	12.3

Comparing Zr loadings on silica for samples treated with Ph₃SiCl and Me₃SiCl at the same wt.% Si/SiO₂, one infers that the ligands around the Si atom do influence the grafted Zr content by steric hindrance. The less sterically demanding ligand Me affords about 20% higher Zr loadings as compared to Ph₃. As discussed for Fig. 1, increasing organosilicon content from 0.30 to 1.00 wt.% Si/SiO₂ leads to reduction in catalyst activity, probably due to destabilization of the active species by the Me ligands. However, it seems that the Me groups afford less deactivation reactions than Ph, since increasing organosilicon content from 0.30 to 1.0 wt.% Si/SiO₂ leads to 57% catalyst activity reduction for Ph₃Si- and only 37% for Me₃Si-modifiers.

Given the observed dependence of Zr loading on silica on the nature of organosilicon modifier, one should expect Me₂SiHCl to yield even higher metal loadings than Me₃SiCl, since it presents a less sterically demanding coordination sphere. However, it rendered the lowest metallocene loadings found in this study.

As Me₂SiHCl presents two potential labile ligands (–Cl and –H), we decided to monitor its reaction at the silica surface by FT-IR (Fig. 3). In Fig. 3b, one observes a band at 2155 cm⁻¹ attributed to $\nu_{\text{Si-H}}$ vibrational modes, besides a band at 2975 cm⁻¹ characteristic of $\nu_{\text{C-H}}$ in CH₃ [43]. According to ionicity data, Si–Cl bonds are more reactive than Si–C or Si–H ones, although stronger, they are more polar, rendering the silicon more susceptible to

attack [47]. Thus, it seems that chloride ligands are preferentially reacting with surface OH groups, rather than the hydride ligand. The Si–Cl bonds absorb between 600 and 550 cm⁻¹, but since silica exhibits a very low transmission below 1000 cm⁻¹, associated to the fact that we employed CaF₂ windows in IR analysis (which have cutoff at 1200 cm⁻¹), $\nu_{\text{Si-Cl}}$ could not be observed. According to Fig. 3b, the residual OH groups on the silica surface are practically not perturbed by the methyl ligands, contrarily to what takes place in the case of phenyl ligands (compare Fig. 3b to Fig. 2b).

After impregnation of 0.12 wt.% Zr/SiO₂ on the silica tablet, the $n\text{BuCp}$ vibrational modes

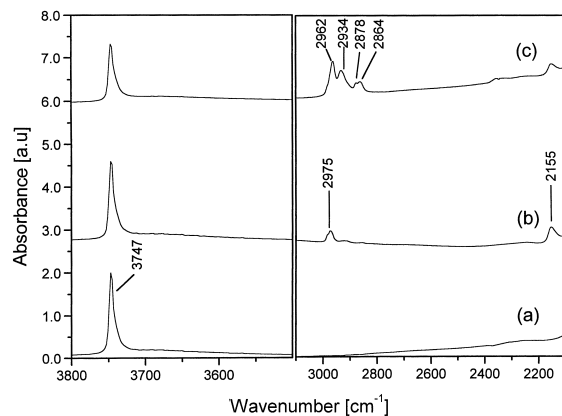


Fig. 3. IR spectra in the 3800–3500 and 3100–2100 cm⁻¹ regions of: (a) SiO₂ dehydroxylated at 723 K for 16 h under vacuum; (b) same as in (a) followed by impregnation at 298 K with a 0.3 wt.% Si/SiO₂ methylchloride solution of Me₂SiHCl. (c) same as in (b) followed by impregnation at 298 K with a 0.12 wt.% Zr/SiO₂ toluene solution of $(n\text{BuCp})_2\text{ZrCl}_2$. The right hand side of the spectra is multiplied by a factor of 3.

appear in wavenumbers similar to those observed in the preceding cases. A decrease in the intensity of the band characteristic of $\nu_{\text{Si-H}}$ (2155 cm^{-1}) suggests that it was partially consumed during metallocene immobilization.

According to these results, the presence of residual Si–H groups on silica might have somehow led mostly to unstable catalyst species, which did not remain chemically bonded to the silica surface. In spite of this fact, the very low amount of grafted metallocene seems to be in a very active form, since catalyst activity for this system is comparable to that of others presenting much higher Zr loadings (see third and fourth columns of Table 1).

Concerning polymer characterization, all systems produced PE with melting (T_m) and crystallization (T_c) temperatures practically constant at $408.5 \pm 0.5 \text{ K}$ and $392.0 \pm 0.8 \text{ K}$, respectively. These temperatures are typical of linear high-density polyethylenes. Table 2 presents weight average molecular weight (M_w), polydispersity index (M_w/M_n) and crystallinity (C) of the PEs produced with the different supported systems. For comparison, data concerning the homogeneous catalyst are also included.

According to Table 2, most of the PEs produced with the supported catalysts present a higher molecular weight than the one obtained with the soluble system. This behavior has al-

ready been observed [46] 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 [47]. It is worth mentioning that polymers with high average molecular weights show better mechanical properties as compared to polymers with low average molecular weights. In the case of Ph_3Si -modified silica, the lower M_w observed for the systems with 0.50 and 1.00 wt.% Si/SiO₂ could be attributed to their lower activity.

Polydispersity values remained in the range 1.9–2.4. PEs produced with the supported systems presented lower polydispersity than those obtained with the soluble catalyst or even with the $(n\text{BuCp})_2\text{ZrCl}_2/\text{SiO}_2$ catalyst, thus indicating that immobilizing this metallocene onto the organosilicon-modified silicas led to generation of polymerization-active species more homogeneous in nature. It is worth mentioning that polymers with narrower molecular weight distribution have greater toughness at low temperatures, and higher resistance to environmental stress cracking.

No special trend could be observed for crystallinity among PEs produced by the different catalyst systems. Only Ph_3Si -modified silica at the 1.0 wt.% Si/SiO₂ level produced PE with crystallinity significantly lower than those observed for other samples.

Table 2

Properties of PEs produced using different $(n\text{BuCp})_2\text{ZrCl}_2$ supported catalysts. Data for the zirconocene in homogeneous milieu are included for comparison.

Organosilicon	Modifier loading (wt.% Si/SiO ₂)	M_w (10^5 g mol^{-1})	M_w/M_n	C (%)
(Bare SiO ₂)	–	2.3	2.4	74
Ph_3SiCl	0.15	2.1	2.2	57
	0.30	3.0	2.2	58
	0.50	1.0	2.0	59
	1.00	1.0	1.9	24
Me_3SiCl	0.30	1.9	2.0	46
	1.00	1.1	2.0	41
Me_2SiHCl	0.30	2.0	1.9	45
(Homogeneous)	–	1.6	2.5	60

4. Conclusion

The purpose of this work was to find a way to keep apart metallocene species on the silica surface, in order to prevent bimolecular deactivation reactions. The chemical modification of SiO₂ with organosilicons prior to zirconocene grafting seems to be a potential approach. The amount of grafted zirconocene is reduced with increasing organosilicon content on silica. In the

tested organosilicon content range, FT-IR monitoring showed that most of the isolated silanol groups are not consumed. Subsequent zirconocene grafting did not lead to a significant consumption of the residual OH groups, probably due to steric hindrance played by the bulky *n*BuCp ligands.

Hereafter, the observation that spacers in suitable concentration between metallocenes and silica increase catalyst homopolymerization activity will be taken as evidence that such support modification stabilizes surface metallocene species, avoiding the bimolecular deactivation reaction.

A less sterically demanding modifier (Me_3SiCl as compared to Ph_3SiCl) was seen to yield higher zirconocene loadings on silica. Nevertheless, Me_2SiHCl , whose Si–H functionality is kept after impregnation, might lead to deactivation of potentially active species, which did not remain grafted on silica. Despite bearing lower metal loadings on silica, this modifier led to catalyst activities comparable to those observed for the other systems. This suggests that the most of the grafted metal in supported catalysts is present in inactive form.

For all modified silicas, impregnation of high amounts of organosilicon onto the support (more than 0.3 wt.% Si/SiO₂) led to low catalyst activity, probably due to deactivation of catalytically active species.

Concerning polymer properties, the organosilicon-modified supported catalysts produced polymers presenting higher M_w and lower molecular weight distribution, indicating, respectively, higher catalyst activity and greater homogeneity in the nature of the polymerization active species as compared to systems based on bare silica.

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