Metallocene catalyst supported on chemically modified silica for production of ethylene–propylene copolymers

Mônica C. Haag, Jairton Dupont, Fernanda C. Stedile, João H.Z. dos Santos[*]

Instituto de Química, Universidade Federal do Rio, Grande do Sul (UFRGS), Av. Bento Gonçalves 9500, Porto Alegre 91509-900, Brazil

Abstract

In the present work $Et(IndH_4)_2ZrCl_2$ was immobilized on silica previously modified with different chemical compounds, namely $VOCl_3$, $SnCl_4$, Bu_3SnH, Me_2SiHCl, polymethylhydrosiloxane (PMHS) and such systems were compared to methylaluminoxane (MAO) pretreated systems. Bu_3SnH-modified silica led to the highest zirconocene grafted content. Zr $3d^{5/2}$ binding energy determined by X-ray spectroscopy (XPS) was shown to increase for $Et(IndH_4)_2ZrCl_2$ supported on silica modified with $VOCl_3$, MAO and Bu_3SnH, suggesting the generation of more electron deficient surface species. All systems were shown to be active in ethylene–propylene copolymerization, presenting higher activity than those prepared by grafting the zirconocene on bare silica. Aging test with MAO-mediated systems showed that the catalyst bearing 2.0 wt.% Al/SiO_2 kept its catalyst activity at least for 3 months after preparation.
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1. Introduction

Blends of ethylene–propylene diene comonomer with propylene (EP(D)M/PP) are a representative part of termoplastic elastomers (TPE) that combine both elastomeric and termoplastic characteristics, i.e. associating rubber-like properties and thermoplastic processability. The worldwide consumption of TPEs was estimated to be ca. 1.3 million tonnes per year in 1998 [1]. EP thermal and mechanical properties depend on mean molecular weight, molecular weight distribution, propylene content and the distribution sequence of propylene units. These properties can be both controlled by the catalyst system and by

polymerization conditions. Conventional processes to produce EP copolymers are based on vanadium or titanium Ziegler-Natta catalysts. Metallocene/MAO catalyst systems have also been tested [2]. In this case, besides usual advantages attributed to metallocene catalysts such as high activity, narrow molecular weight distribution and low residual metal content in final products [3], other additional advantages have been claimed in the case of copolymerization, namely higher comonomer incorporation and more uniform comonomer distribution [4].

Extensive research in metallocene chemistry has shown that polymer characteristics can be predicted and controlled by choosing the suitable coordination sphere around the metal center [5]. Metallocenes such as Cp_2ZrCl_2 produced more random EP copolymers than those obtained by vanadium or titanium conventional Ziegler-Natta catalysts [6]. On the other hand,

* Corresponding author. Tel.: +55-51-3316-7238;
fax: +55-51-3319-1749.
E-mail address: jhzds@iq.ufrgs.br (J.H.Z. dos Santos).

metallocene systems such as $bis(2\text{-}PhInd)ZrCl_2$ in the presence of methylaluminoxane (MAO) promoted random or slightly blocky incorporation of comonomers [7]. Other systems based on $Me_2C(3\text{-}RCp)(Flu)ZrCl_2$ (R = H, Me, *i*Pr, *t*Bu) followed different mechanisms according to the size of the substituent and of the nature of precursor. For R = *i*Pr, an alternating mechanism for EP copolymerization has been observed. For R = H and Me, the authors concluded that copolymerization proceeds via chain migratory insertion whereas a retention copolymerization mechanism was founded for R = *t*Bu [8]. Moreover, the system $Et(1\text{-}Ind)(9\text{-}Flu)ZrCl_2$ afforded an alternating ethylene–propylene copolymer [9].

Metallocene/MAO catalysts are soluble, being therefore unsuitable for direct application in modern industrial gas phase or slurry polymerization processes, which require heterogeneous catalysts in a particle form. The heterogeneization of metallocene catalysts is an important issue, and it has been investigated both by academic and industrial researchers. Many routes have been proposed in the literature, involving different supports, different immobilization conditions or support chemical modification [10]. Among them, the use of organosilicon spacers has been proposed as an alternative to overcome the lower activity exhibited by supported metallocene and attributed in part to the steric effect played by the silica surface, which acts as a huge ligand [11]. The use of such spacers, which can lead to zirconocene species grafted farther from the support surface, has been claimed to afford systems bearing higher catalyst activity than those supported on bare silica.

In previous studies [12,13], we reported some results concerning the modification of silica surface with smaller organosilicon compounds such as Ph_3SiCl, Me_3SiCl and Me_2HSiCl which acted as *horizontal spacers*, keeping catalyst site far from each other, reducing the probability of bimolecular deactivation reactions. The use of these organosilicon compounds was shown to lead to more active supported systems in comparison to those obtained by grafting metallocene directly on bare silica [12]. Such interactions between zirconocene, silica and *horizontal spacers* were also modeled [13]. Silica modified with Me_2SiCl_2, followed by MAO impregnation prior to Cp_2ZrMe_2 grafting was also reported to increase catalyst activity in ethylene polymerization [14].

In the present study, we report the results concerning the immobilization of $Et(IndH_4)_2ZrCl_2$ on silica chemically modified with Bu_3SnH, Me_2SiHCl, $VOCl_3$, polymethylhydrosiloxane (PMHS) and $SnCl_4$. For comparative reasons, MAO-modified silica containing 2.0, 4.5, and 8.6 wt.% Al/SiO_2 were also used as supports. The resulting catalyst systems were characterized by inductive-plasma optical emission spectroscopy (ICP-OES), Rutherford backscattering spectrometry (RBS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS). The supported catalysts were tested in EP copolymerization, using MAO as cocatalyst. The resulting copolymers were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and ^{13}C nuclear magnetic resonance (^{13}C NMR).

2. Experimental part

2.1. Chemicals

All products were manipulated using the Schlenk technique. Catalyst precursor $Et(IndH_4)_2ZrCl_2$ and methylaluminoxane (MAO) were supplied by Witco, while Silica grade 948 was purchased from Grace (Baltimore, USA). Bu_3SnH, Me_2SiHCl, PMHS and $SnCl_4$ were supplied from Aldrich and $VOCl_3$ was donated by Nitriflex S.A. (Triunfo, Brazil). Polymerization grade ethylene (Copesul S.A., Triunfo, Brazil) and propylene (White-Martins, Porto Alegre, Brazil) were dried through columns of 0.4 nm molecular sieve. Toluene (Nuclear, Porto Alegre, Brazil) was dried by refluxing over metallic sodium followed by distillation under argon atmosphere.

2.2. Catalyst preparation

Silica was activated at 723 K for 18 h under vacuum ($<10^{-4}$ mbar) prior to chemical modification by impregnation with MAO (initial impregnation toluene solution containing MAO corresponding to 2.0–12.0 wt.% Al/SiO_2), Bu_3SnH (3 wt.% Sn/SiO_2), Me_2SiHCl (0.3 wt.% Si/SiO_2), $VOCl_3$ (4.5 wt.% V/SiO_2), PMHS (5.0 wt.% Si/SiO_2) or $SnCl_4$ (0.1 wt.% Sn/SiO_2), followed by solvent removal by vacuum. This initial solution concentration was

chosen based on previous studies, in which saturation levels or adsorption isotherms for such compounds were determined [12,15,16]. In the second step, Et(IndH$_4$)$_2$ZrCl$_2$ toluene solution corresponding to 1.5 wt.% Zr/SiO$_2$ was added to the corresponding modified silica. The slurry was magnetically stirred for 1 h at 303 K, filtered, washed with toluene (15 × 2 ml) and vacuum dried in accordance to previous protocol [17,18].

2.3. Catalyst characterization

DRIFTS measurements were made in a BOMEM FTIR spectrophotometer (MB-102, Quebec, Canada) at 298 K, coadding 32 scans at a resolution of 4 cm^{-1}. The measurements were restricted to 4000–2600 cm^{-1} region. The samples were analyzed as powder in a DRIFT accessory equipped with sampling cups under inert atmosphere. The spectra were collected as reflectance units and transformed to Kubelka–Munk units.

XPS measurements were performed in PHI 5600 Esca System (Φ Physical Electronics), using Al monochromated 2 mm filament (Al Kα radiation, 1486.6 eV) at 300 W. Spectra were run at room temperature in low-resolution (pass energy 235 eV) in the range of 1000–0 eV and in high-resolution (pass energy 23.5 eV) modes for the Si 2p, Al 2p and Zr 3d regions with resolution of 0.05 eV. Samples were mounted as thin films on an adhesive copper tape in a glove box. Takeoff angle was 75°. All binding energy values were charge referenced to the Si 2p at 103.3 eV. Measurement details and data treatment are reported elsewhere [19].

2.4. Polymerization reactions

The polymerization reactions were carried out in a 1 l glass reactor using toluene as solvent and a mass of catalyst system corresponding to ca. 2 × 10^{-5} M. The catalyst and cocatalyst (MAO, 2 × 10^{-2} M) were introduced in this order into the reactor containing 0.3 l of toluene under positive pressure of a mixture of ethylene and propylene (60/40 in mass, controlled by mass flowmeters at 328 K). After 30 min, the reaction was quenched by the addition of ethanol. The polymer was collected, washed with ethanol and vacuum dried at room temperature for 16 h. This procedure

for ethylene and propylene copolymerization and the details concerning to reaction setup and modeling as well as consumption profiles were described elsewhere [20,21].

2.5. Polymer characterization

Molar masses and molar mass distributions were investigated with a high-temperature GPC instrument (Waters, 150 CV Plus, USA) equipped with an optic differential refractometer and three Styragel HT type columns (HT3, HT4, HT6) with exclusion limit 1 × 10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1 l min^{-1} and the analyses were performed at 413 K. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with standard polyethylenes and polypropylenes.

Propylene incorporation and polymer microstructure was determined by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra were obtained at 353 K in a Varian Inova 300 equipment (Varian Associates, USA) operating at 75 MHz. Spectra were taken with a 70° flip angle, an acquisition time of 1.5 s and a delay of 4.0 s. Chemical shifts were referenced internally to the major backbone methylene resonance (taken as 30.00 ppm from Me$_4$Si), calculated according to the rules of Linderman and Adams [22]. These theoretical chemical shifts and their correlated triads are listed elsewhere [23]. The triads concentration was calculated using spectral regions as proposed by Randall [24]. Sample solutions were prepared in *o*-dichlorobenzene and deuterated benzene (20 vol.%) in a 5 mm sample tube. The deuterated solvent was used to provide the internal lock signal.

3. Results and discussion

In previous studies, the use of organosilanes aimed at generating more spaced zirconocene species on silica surface. The amount of impregnated organosilane should be enough to consume a small amount of silanol groups, leaving residual OH groups available for further reaction with (*n*BuCp)$_2$ZrCl$_2$ [12]. In the present study, we extended the same approach for other compounds. PMHS, VOCl$_3$, SnCl$_4$ and Bu$_4$Sn were impregnated onto silica surface in concentration

Table 1
Supported catalyst system and elemental content determined by XPS

Symbol	Catalyst system	Elemental (atom%)
IndH$_4$	Et(IndH$_4$)$_2$ZrCl$_2$/MAO	–
SiO$_2$	Et(IndH$_4$)$_2$ZrCl$_2$/SiO$_2$	0
Me$_2$SiHCl	Et(IndH$_4$)$_2$ZrCl$_2$/Me$_2$HSiCl/SiO$_2$	0.9 (Si)
PMHS	Et(IndH$_4$)$_2$ZrCl$_2$/ Me$_3$SiO[SiHMeO]$_{35}$Me$_3$SiH/SiO$_2$	0.7 (Si)
Bu$_3$SnH	Et(IndH$_4$)$_2$ZrCl$_2$/Bu$_3$SnH/SiO$_2$	0.6 (Sn)
SnCl$_4$	Et(IndH$_4$)$_2$ZrCl$_2$/SnCl$_4$/SiO$_2$	0.5 (Sn)
VOCl$_3$	Et(IndH$_4$)$_2$ZrCl$_2$/VOCl$_3$/SiO$_2$	0.5 (V)
2.0% Al	Et(IndH$_4$)$_2$ZrCl$_2$/MAO/SiO$_2$	29.0 (Al)
4.6% Al	Et(IndH$_4$)$_2$ZrCl$_2$/MAO/SiO$_2$	35.0 (Al)
8.6% Al	Et(IndH$_4$)$_2$ZrCl$_2$/MAO/SiO$_2$	44.0 (Al)

much lower than that corresponding to their saturation level. The resulting solids were used as support for grafting Et(IndH$_4$)ZrCl$_2$. Table 1 reports all the prepared supported metallocenes and the final element content (Si, Al, V, or Sn) correspondent of the chemical modifier determined by XPS analysis.

According to Table 1, organosilane compound systems afforded 0.7–0.9% Si. Lower atom contents were observed in the case of tin derivatives or in the case

of VOCl$_3$. On the other hand, higher atomic percentage were observed for MAO-modified systems, being 8.6 wt.% Al/SiO$_2$ the content corresponding to silica saturation in MAO, as determined previously [15]. It is worth mentioning that the labels 2.0, 4.6, and 8.6% in the case of MAO-modified systems correspond to final Al content 29, 33, and 44 wt.% Al/SiO$_2$, determined by ICP-OES analysis.

Fig. 1 compares Zr loading in the supported catalysts determined through three different techniques, namely XPS, ICP-OES and RBS. The former is essentially a surface technique where the sampling depth is approximately 3–4 nm. Therefore, the relatively higher Zr content determined by XPS analysis suggests that the metallocene is indeed at the uttermost external surface. Zr contents determined by ICP-OES and RBS are comparable, the latter being a little higher. Metal content determination by ICP-OES analysis demands a digestion step and extraction of the metal from the support, leading to some preparative and sampling errors. On the other hand, in the RBS analysis, the samples were directly compared as solid pellets.

According to Fig. 1 and considering the results from both ICP-OES and RBS, we observe the same trend among the different systems concerning the
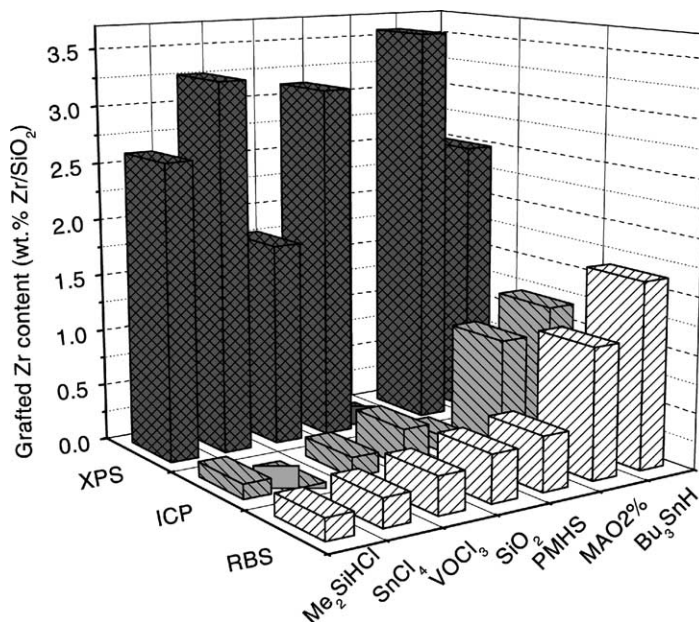

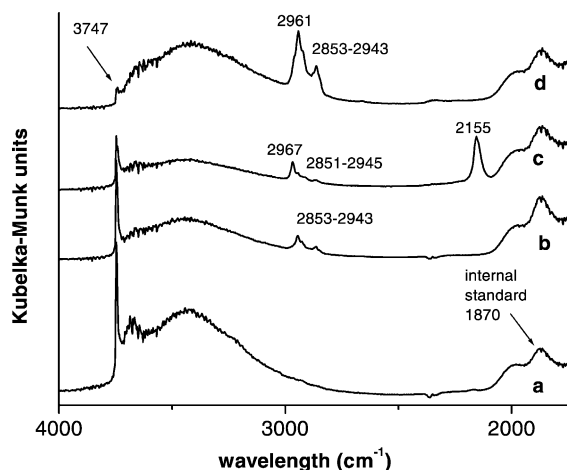Fig. 1. Zr loading in the supported systems determined by XPS, ICP-OES and RBS.

Fig. 2. DRIFTS spectra of the prepared systems: (a) pure silica, (b) Et(IndH4)2ZrCl2/SiO2, (c) Et(IndH4)2ZrCl2/Me2SiHCl/SiO2, and (d) Et(IndH4)2ZrCl2/Bu3HSn/SiO2.

final grafted Zr content. Bu3HSn is the spacer that affords the highest Zr loading, followed by the MAO-mediated system. Grafting reaction of some of these systems was monitored by DRIFTS analysis (Fig. 2). Silica surface after thermal treatment is characterized by a strong band at $3747 \, cm^{-1}$ attributed to $\nu_{(O-H)}$ from isolated silanol groups. Larger bands at the lower wavenumber sites suggest the presence of other silanol groups interacting by intermolecular forces. After grafting Et(IndH4)ZrCl2 we can observe the reduction in intensity of the band placed at $3747 \, cm^{-1}$ and appearance of new bands at $2950–2850 \, cm^{-1}$ attributed to CH3 and CH2 stretching of the terahidroindenyl counterpart: 2945, 2924, 2913, 2863, and $2851 \, cm^{-1}$. The aromatic vibrations from Cp at $3060–3050 \, cm^{-1}$ might be covered by the large band centered at $3600 \, cm^{-1}$ [25].

In the case of Me2SiHCl-modified silica we can also observe reduction of isolated silanol band. Besides the bands attributed to the zirconocene counterpart, bands situated at 2155 and $905 \, cm^{-1}$ (not shown in Fig. 2) can be attributed respectively to $\nu_{(Si-H)}$ and $\delta_{(Si-H)}$ of Me2SiHCl suggesting that during surface reactions, Si–Cl might be preferentially consumed. The reaction of Me2SiHCl with isolated silanol groups is already reported in the literature [26], and HCl is liberated to form the species. Recent theoretical studies did not exclude the possibility of interaction between

this organosilicon compound and (nBuCp)2ZrCl2 [13].

The reaction of Bu3SnH-modified silica was also monitored by DRIFTS (Fig. 2). In this case, the reduction of isolated silanol groups band is very significant, but a large band centered at $3500 \, cm^{-1}$ is also observed suggesting that the reduction in band intensity might also be attributed not only to OH consumption but also to perturbation of isolated silanol groups by the spacers. The intense bands in the $\nu_{(CH)}$ stretching region $(2950–2850 \, cm^{-1})$ contain vibrational bands attributed to nBu ligands. The $\nu_{(Sn-H)}$ stretching at $1837 \, cm^{-1}$ [16] was not observed confirming that this bond disappeared during the immobilization on silica. Similar reaction between Bu3SnH and silica surface is already described in the literature [27].

Similar results were observed in the case of the other surface modifier. It is worth mentioning that in the case of PMHS, bands attributed to $\nu_{(Si-H)}$ at $2155 \, cm^{-1}$ and $\delta_{(Si-H)}$ at $905 \, cm^{-1}$, indicate that residual Si–H are still available for zirconocene grafting. Taking into account the DRIFTS results and data from the literature, the most probable surface species generated by the reaction of organosilanes, tin derivatives and VOCl3 and silica surface are proposed in Scheme 1. Monodentate species for Me2SiHCl (I) and Bu3SnH (II) were also reported in the literature [26,27]. In the case of VOCl3 and SnCl4, surface reaction must proceed by production of HCl, generating species III and IV. Bidentated species by the consumption of an additional Cl in the case of the VOCl3 are not favored [28]. The reaction of PMHS with silica is more prone to lead to structure V with H2 evolving and involving probably more than one anchorage site. Residual Si–H groups are still available.

The silanol consumption after zirconocene grafting was semi-quantitatively evaluated by measuring the isolated silanol band area $(3747 \, cm^{-1})$ and normalized by the area of the band placed at $1870 \, cm^{-1}$ which is attributed to structural harmonic vibration of silica that remains unchanged by the chemical treatments [29]. Fig. 3 reports the total elemental concentration (Zr from zirconocene and V, Si, or Sn from the chemical spacers) determined by XPS and the percentage of consumed OH, assuming the silanol groups in the thermal pretreated silica support as 100%. According to Fig. 3, a direct trend between grafted content and percentage of consumed OH groups can be observed
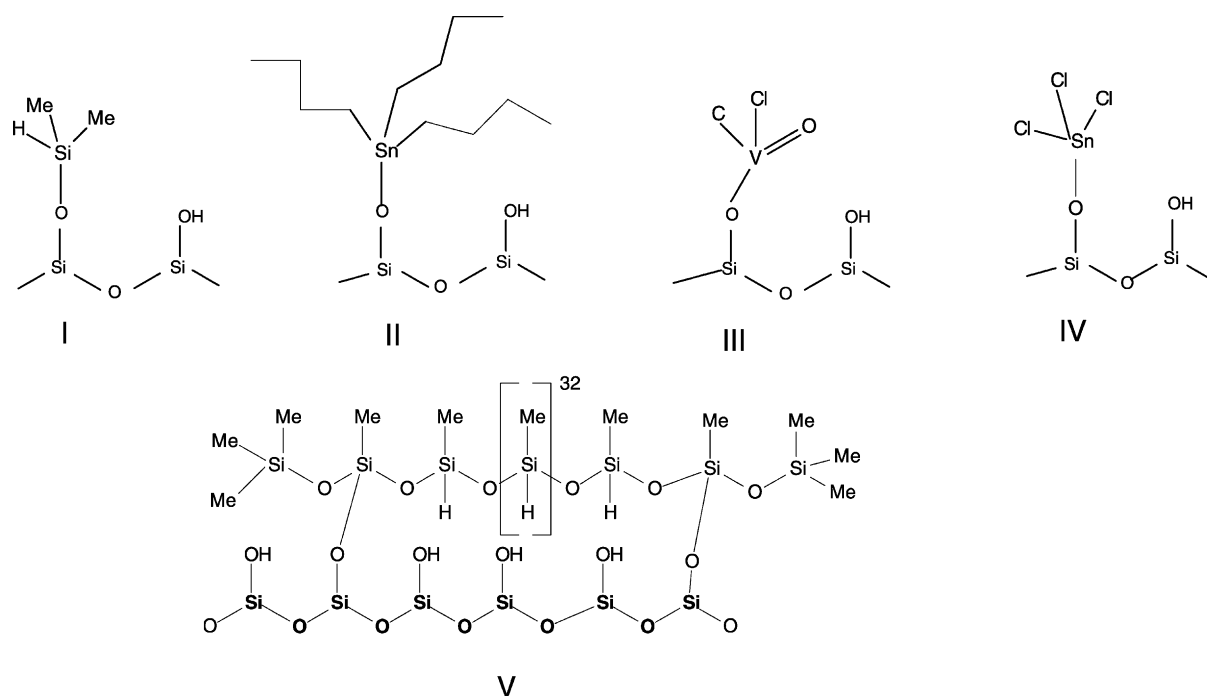
Scheme 1.

independent of the chemical modifiers, except in the case of Bu$_3$SnH. The interaction between hydrogen of CH$_3$ from nBu groups and the residual OH groups is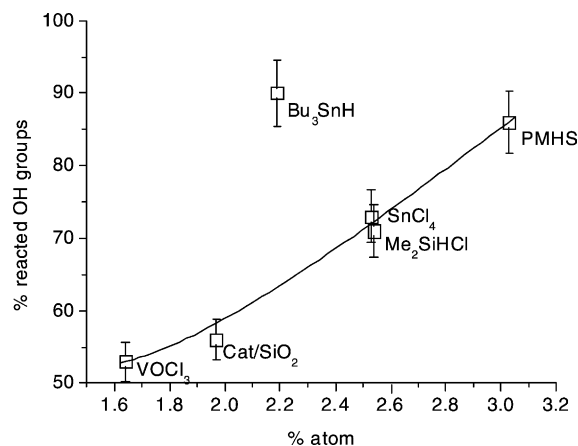 already cited in the literature [24]. Therefore, it is very likely that such interaction should lead to a reduction of silanol band intensity and an increase of the large band at 3500 cm^{-1} corresponding to OH groups interacting through OH bridges (in the case H from the nBu groups and OH from silica surface). Then the reduction in silanol isolated groups does not necessarily signify that the silanol groups have been consumed, but conversely perturbed.

All the systems were evaluated in ethylene–propylene copolymerization. As we can see in Fig. 4, excepting the PMHS-modified systems, all the systems modified with *horizontal spacers* afforded catalyst systems more active than those resulting from zirconocene grafting on bare or on MAO-modified silica. The highest activity was observed for silica modified with Me$_2$SiHCl. Neither specific trend between the nature of the chemical modifier (V, Si, or Sn compound) and catalyst activity, nor grafted Zr content and catalyst activity was observed.

The corresponding EP resulting copolymers were characterized by GPC. Fig. 5 shows the mean molecular weight (M_w) and polypropylene molar fraction for the copolymers produced with the different supported

Fig. 3. Surface coverage for silica-modified catalysts. Atom percentage is referred to the sum of Zr and Si, Sn, or V from the spacer.
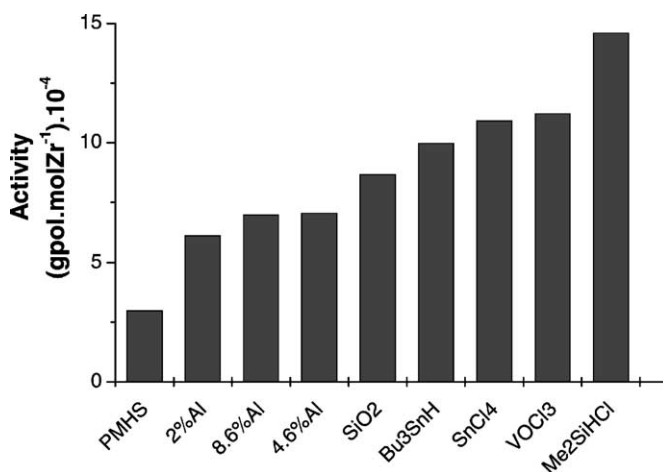
Fig. 4. Catalyst activity of the supported systems in ethylene–propylene copolymerization using MAO as cocatalyst.

systems. As we can observe, M_w roughly follows an inverse trend of comonomer incorporation. The dependence between these two factors is already reported for ethylene–propylene copolymerization with metallocene catalysts in homogeneous milieu [30–32]. The system pretreated with Bu$_3$SnH and SnCl$_4$ presented the highest propylene incorporation, followed by those pretreated with MAO. The effect of surface MAO content on the propylene incorporation on EP copolymers are also reported in the literature in the case of EtInd$_2$ZrCl$_2$-supported catalysts [18].

Table 2 shows the mean molecular weight, polydispersity index and melting point of the resulting copolymers. Molecular weight remained roughly constant among the EP copolymers obtained with the supported systems, being higher than that corresponding to the copolymer produced with the homogeneous systems. This behavior has been 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 [33]. Polydispersity index did not change very much among the produced copolymers. The DSC curves for the copolymers showed a
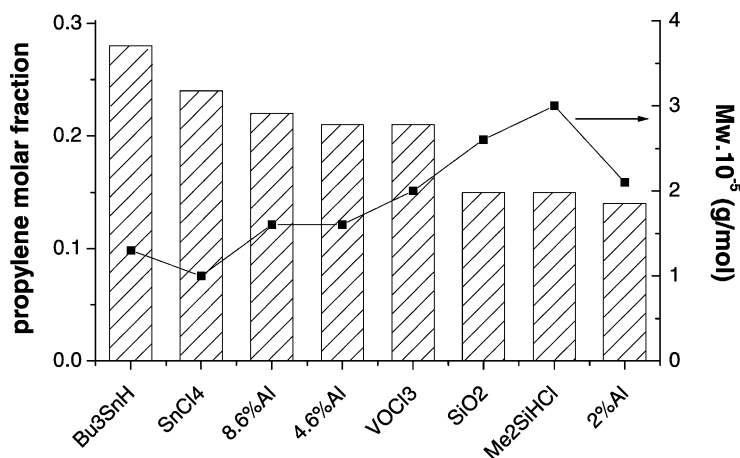

Fig. 5. Propylene content and mean mass molecular weight of the resulting copolymers produced by the supported systems.

Table 2
Copolymer characteristics

Symbol	$M_w \times 10^{-5}$ (g mol^{-1})	M_w/M_n	T_m (°C)
IndH$_4$	0.5	2.1	[a]
SiO$_2$	2.6	3.2	47
Me$_2$SiHCl	3.0	2.0	54
PMHS	2.0	3.7	54
Bu$_3$SnH	1.3	2.0	39
SnCl$_4$	1.0	2.1	56
VOCl$_3$	2.0	2.0	58
2.0% Al	2.0	2.0	55
4.6% Al	1.6	2.0	51

[a] $T_g = -52$ °C.

behavior compatible with the comonomer content of the samples. A broad melting band with the melting point pointed out in Table 2 was observed for these copolymers. The glass transitions were not clearly observed for the supported systems, probably due to the low comonomer incorporation. The glass transition temperature was observed just for the homogeneous system.

Fig. 6 presents the binding energy (BE) of Zr $3d^{5/2}$ electrons for Et(IndH$_4$)ZrCl$_2$, (IndH$_4$) and for the supported systems. The energy of the pure complex (IndH$_4$) is very close to that reported from Gassman for [Cp$_2$ZrCl]O derivatives (181.5 eV) [34]. All the supported systems exhibited a higher Zr BE in comparison to that observed in the case of IndH$_4$

(181.7–183.0 eV), suggesting that grafting the complex on silica increases the electropositive character of the Zr atom. Silica modified with Me$_2$SiHCl, SnCl$_4$ and PMHS afforded supported zirconocene catalysts which Zr BE is close to that observed in the case of grafting directly on silica support. The use of VOCl$_3$ in the support lead to more eletropositive Zr centers, close to that observed in the case of supported zirconocene on MAO-modified silicas. Finally, the highest electropositive character was determined in the case of Bu$_3$SnH and MAO-modified silica (8.6 wt.% Al/SiO$_2$). In a previous study, we observed a positive correlation between decreasing of the Zr $3d^{5/2}$ electron binding energy and the increment of catalyst activity in the case of Et(Ind)$_2$ZrCl$_2$/MAO/SiO$_2$ [18]. Conversely in the present systems, no clear relation could be established. It is worth mentioning that comparing Zr $3d^{5/2}$ BE and propylene incorporation, we can observe also the highest comonomer incorporation for the Bu$_3$SnH system. It seems that higher Zr $3d^{5/2}$ binding energies, consequently a more electropositive Zr atom, permits a higher incorporation from the richest electron olefin, the propylene.

Aging tests were performed with five supported systems (Fig. 7). Three of the systems presented a considerable initial activity drop 20 days after preparation: those bearing Bu$_3$Sn-modified silica and those prepared on MAO-modified silicas (4.6 and 8.6 wt.%
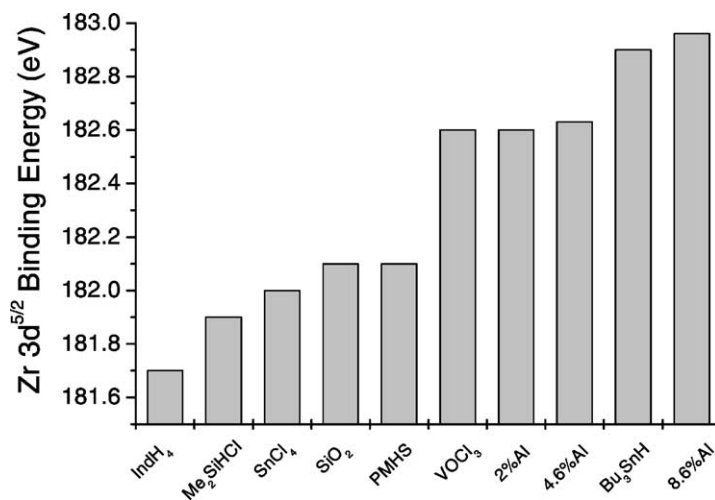

Fig. 6. Zr $3d^{5/2}$ electron binding energy for the supported systems.
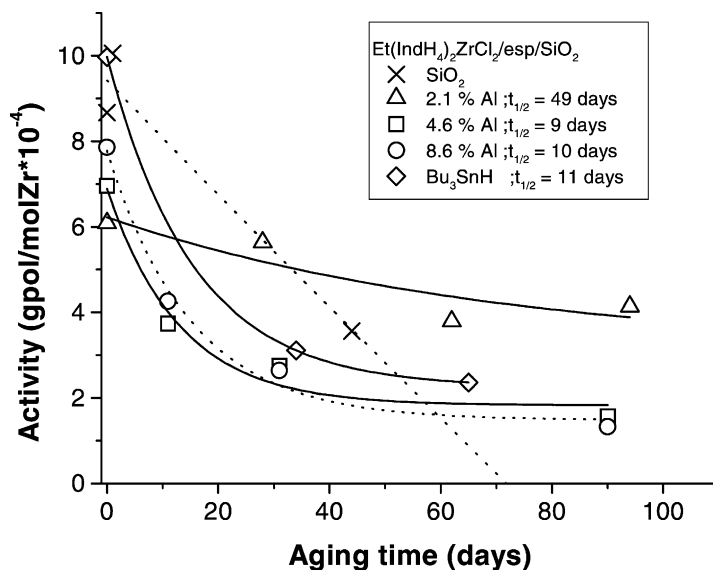
Fig. 7. Effect of catalyst aging of some supported systems.

Al/SiO$_2$). The highest stability was observed for the systems containing 2 wt.% Al, that showed a lower initial activity, which was kept constant for at least 90 days. It seems that the presence of these compounds (Bu$_3$Sn and MAO groups) might somehow react with the surface zirconocene species leading to deactivation reactions.

4. Conclusions

Chemical modification of silica with Me$_2$SiHCl, SnCl$_4$ and VOCl$_3$ led to lower grafted Zr content probably due to partial consumption of silanol groups, reducing therefore grafting sites on silica surface. Conversely PMHS, probably due to the presence of Si–H groups in its structure might afford a higher grafted metal content. Bu$_3$SnH afforded the highest metal content among the studied systems. Besides such systems led to the highest propylene incorporation being characterized by Zr species bearing high BE, i.e. strong electrodeficiency.

The presence of these horizontal spacers might influence not only the spacing among surface species, but also the electronegativity in the environment. Systems using MAO-modified silica as supports, bearing 2.0 wt.% Al/SiO$_2$ were shown to keep active for at least 90 days.

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