Ethylene homo- and copolymerization using (nBuCp)$_2$ZrCl$_2$ grafted on silica modified with different spacers

Griselda Barrera Galland*, João H.Z. dos Santos, Fernanda C. Stedile,
Paula Palmeira Greco, Adriano D. Campani

Instituto de Química, Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalves 9500, Porto Alegre 91501-970, Brazil

Abstract

(nBuCp)$_2$ZrCl$_2$ was grafted on a series of modified silica and evaluated in ethylene/1-hexene copolymerization and their performance was compared with the homogenous system and with that resulting from its immobilization on bare silica. Silica was modified by polymethylhydrosiloxane (PMHS), Me$_3$SiCl, Ph$_3$SiOH, SnCl$_4$, isodrin and aldrin. (nBuCp)$_2$ZrCl$_2$ grafted on PMHS-modified silica afforded the catalyst with the highest activity. Comonomer incorporation, melting point and polydispersity was shown to be dependent on the catalyst nature. Bimodality was observed in the case of ethylene homopolymerization employing PMHS-silica-based catalysts.
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1. Introduction

Metallocene catalysts activated by methylaluminoxane (MAO) produce linear low density polyethylene (LLDPE) with high activities and controlled microstructure [1,2]. LLDPE obtained by copolymerization between ethylene and α-olefins is a material of high industrial importance [3]. The amount of α-olefin can control polymer chain branching, which leads to materials with different melting temperatures, crystallinities and densities. Production of LLDPE is increasing 11.3 tonne per year [4]. In spite of the advantages of metallocene catalysts, LLDPE is still mainly produced by Ziegler-Natta catalysts in slurry or in gas-phase processes. The main constraints to the adoption of metallocene catalysts in industry are the difficulties in materials processability due to narrow molecular weight distribution, the need for high amounts of MAO to activate the metallocenes, and the fact that the process is homogeneous. An approach to reduce the amount of MAO and to adapt metallocenes to industry is immobilizing them on inert carriers to be used in slurry or in gas-phase processes [5]. Many approaches for metallocene immobilization have been de-scribed in the literature, mainly employing silica as supports [6–8]. Among these approaches, we can cite the use of spacers [9]. The silica surface itself plays the role of a huge ligand, hindering the access of the monomer to the center of the support particle, reducing catalyst activity. Silicas have been chemically modified with spacers between the silica surface and the metallocene species. In a previous study, we evaluated the role of different organosilicon compounds differing in the coordination sphere as silica modifiers [10]. The resulting supports were employed for (nBuCp)$_2$ZrCl$_2$ grafting and exhibited twice the activity of this metallocene supported on bare silica. Previous consumption of silanol sites with these compounds prior to zirconocene grafting generates more spaced catalyst species. It is worth mentioning that in homogeneous systems, bimolecular deactivation reactions are responsible for the loss of activity. Therefore, the increase in catalyst activity in ethylene homopolymerization was attributed to generation of more spaced catalyst species, which were less prone to bimolecular deactivation reactions. The role of organosilanes as *horizontal spacers* was confirmed by molecular modeling [11]. Similar behavior was observed in the case of chemical modifiers such as polymethylhydrosiloxane (PMHS) in ethylene homopolymerization [12] and of some organosilanes and organostannanes in ethylene–propylene copolymerization [13].

* Corresponding author. Tel.: +55-51-3316-7313;
fax: +55-51-3316-7304.
E-mail address: griselda@iq.ufrgs.br (G.B. Galland).

(nBuCp)$_2$ZrCl$_2$ has been compared with other zirconocenes such as (R)ZrCl$_2$ (R = (i-BuCp)$_2$, (n-BuCp)$_2$, rac-Et(Ind)$_2$ and rac-Et(IndH$_4$)$_2$), immobilized on bare silica and was shown to present the highest catalytic activity in ethylene/1-hexene copolymerization [14].

In the present work, silica was modified with polymethylhydrosiloxane, chlorotrimethylsilane (Me$_3$SiCl), triphenylsilanol (Ph$_3$SiOH), tin(IV) chloride (SnCl$_4$), 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-$endo$,$endo$-1,4:5,8-dimethanonaphthalene (isodrin) and 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-$endo$,exo-1,4:5,8-dimethanonaphthalene (aldrin). The resulting solids were employed as supports for the immobilization of (nBuCp)$_2$ZrCl$_2$. For comparison, bare silica was employed as support. The resulting catalysts were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and Rutherford backscattering spectrometry (RBS). Catalysts were evaluated in ethylene/1-hexene copolymerization and the polymers were characterized in terms of comonomer incorporation, melting temperature, crystallinity, molecular weight and molecular weight distribution.

2. Experimental

2.1. Materials

Silica (Grace 948, 255 m^2 g^{-1}) was activated by heating under vacuum ($P < 10^{-4}$ mbar) for 16 h at 450 °C. MAO (Witco, 10.0 wt.% toluene solution), (nBuCp)$_2$ZrCl$_2$ (Aldrich), polymethylhydrosiloxane (Aldrich), Me$_3$SiCl (Aldrich), aldrin and isodrin (Aldrich), Ph$_3$SiOH (Aldrich) and SnCl$_4$ (Aldrich) were employed as received. Ethylene and argon (White Martins) were dried and deoxygenated by passage through columns of BTS and activated molecular sieves (13 Å) prior to use. Pure grade toluene were deoxygenated and dried by standard techniques.

2.2. Support modification and catalyst grafting

All experiments were performed under inert atmosphere using the Schlenk technique. Chemically modified supports were prepared by impregnating 1.0 g of activated silica with a toluene solution of organosilicon corresponding to 0.15–8.0 wt.% Si/SiO$_2$ in the case of PMHS, 0.3 and 1.0 wt.% Si/SiO$_2$ for Me$_3$SiCl; 5.0 wt.% Sn/SiO$_2$ in the case of SnCl$_4$ and 0.3 wt.% for isodrin and aldrin were employed. Impregnation reactions were performed at room temperature for 30 min. The solvent was then removed under vacuum, a toluene solution of (nBuCp)$_2$ZrCl$_2$ corresponding to 1.5 wt.% Zr/SiO$_2$ was added, and the resulting slurry was stirred for 1 h at 80 °C and then filtered through a fritted disk. The resulting solids were washed with 15× 2.0 cm^3 of toluene and dried under vacuum for 4 h. An analogous procedure was employed for supporting the catalyst onto bare SiO$_2$, but in this case without chemical modification of the support. Such methods have shown to afford stable supported metallocene systems [15].

2.3. Polymerization reactions

The polymerization reactions were performed using a 1 l glass reactor equipped with a mechanical stirrer and a controlled temperature bath. Reactions were carried out at 60 °C for 30 min using ethylene pressure of 1.6 bar. The reactor was initially treated for 20 min with 600 ml of hexane and 4 ml of trimethylaluminum (TMA) under argon atmosphere. Then hexane was substituted by freshly distilled toluene and MAO solution corresponding to [Al]/[Zr] = 2500 was added. Argon was replaced by ethylene. Finally, a catalyst slurry in toluene containing 1.9 × 10^{-6} mol was added. In the case of copolymerization reactions, 0.38 M of 1-hexene was added. After the reaction, the polymer was isolated by precipitation in a methanol/HCl solution. The polymer was filtrated and dried to constant weight.

2.4. Characterization of the support

2.4.1. Rutherford backscattering spectrometry (RBS)

Zirconium loadings in catalysts were determined by RBS using He$^+$ beams of 2.0 MeV incident on homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems. During analysis, the base pressure in the chamber was kept in the 10^{-7} mbar range using membrane (to prevent oil contamination of the sample) and turbo molecular pump. The method is based on the determination of the number and the energy of the He$^+$ ions particles which are elastically scattered by 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$_2$. For an introduction to the method and applications of this technique, see [16,17].

2.4.2. Diffuse reflectance infrared spectrometry (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^{-1}. This study was restricted to the mid-IR region (4000–2000 cm^{-1}) due to strong bulk absorption of the silica in low wavenumber region. In this region, 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 a nitrogen atmosphere.

2.5. Characterization of the polymers

Molar masses and molar mass distributions were measured with a Waters CV plus 150C high-temperature GPC instrument, equipped with viscometrical detector, and three
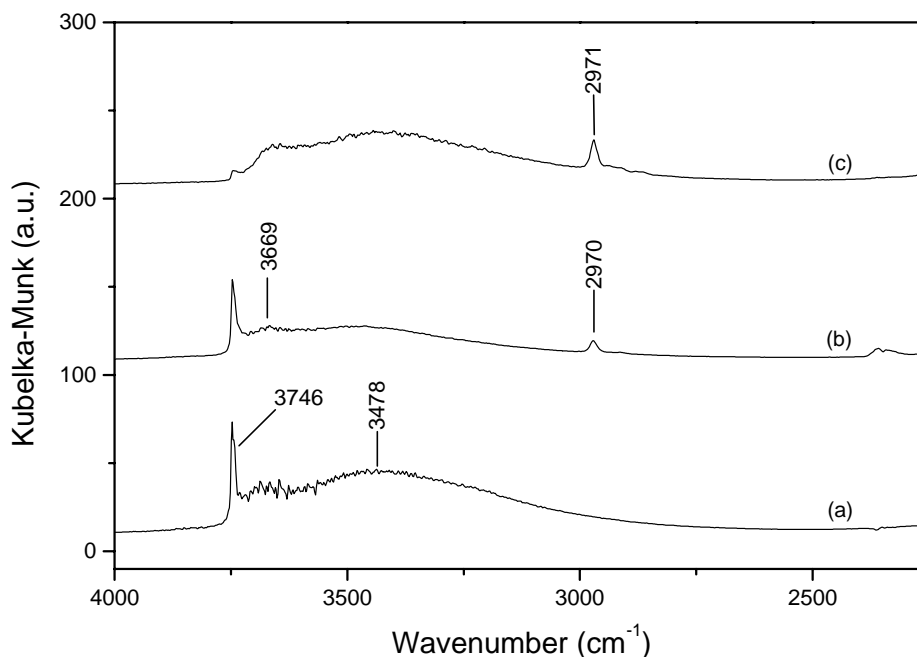
Styragel HT type columns (HT3, HT4 and HT6) with exclusion limit 1×10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of $1 \, cm^3 \, min^{-1}$. The analyses were performed at $140 \, °C$. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low density polyethylenes and polypropylenes.

Polymer melting points (T_m) and crystallinities (χ_c) were determined using differential scanning calorimeter (Polymer Laboratories DSC) calibrated with indium, at a heating and cooling rate of $10 \, °C \, min^{-1}$ in the temperature range 30–160 °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.

^{13}C NMR was employed to determine the composition and sequence distribution of the copolymers according to procedures in the literature [18]. The ^{13}C NMR spectra were recorded at 90 °C using a Varian 300 spectrometer operating at 75 MHz. Solutions of the copolymer were prepared in *o*-dichlorobenzene and benzene d$_6$ (20 v/v) Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s and a delay of 4.0 s. Under these conditions, the spectra are 90% quantitative if only carbon atoms that have a relaxation time (T_1) less than to 2.0 s are taken into account [19].

3. Results and discussion

Silica silanol groups react with compounds such as organometallic chlorides, hydrides and alkoxides through the elimination of HCl, H_2 or alcohol. A similar reaction occurs in the immobilization of (nBuCp)$_2$ZrCl$_2$ onto silica. Thus, surface reaction between chemical modifiers prior to zirconocene grafting leads to a prior consumption of some silanol groups. Grafting zirconocene catalysts on these modified supports engender more widely spaced surface metallocene species. Such an approach might hinder bimolecular deactivation reactions between zirconocene centers, resulting in more active catalysts systems.

PMHS is an oligomer containing Si–H groups that can react with silica silanol groups, as well as with zirconocenes such as (nBuCp)$_2$ZrCl$_2$ eliminating HCl as is shown in

Table 1
Zr contents resulting in different PMHS-modified silicas determined by RBS

Si/SiO$_2$ (%)	Zr/SiO$_2$ (%)
0.0	0.85 [12]
0.15	0.37 [12]
0.30	0.36 [12]
0.50	0.33 [12]
1.00	0.33 [12]
3.00	0.28 [12]
5.00	0.33
8.00	0.32

Scheme 1. In previous work, we observed that for PMHS contents between 0.15 and 3.00 wt.% Si/SiO$_2$, the amount of metallocene bound to the silica surface decreased as PMHS content increased [12]. In the present study, higher PMHS content, namely 5.00 and 8.00 wt.% Si/SiO$_2$, were employed. Table 1 reports the nominal PMHS content. In all systems, (nBuCp)$_2$ZrCl$_2$ was supported by grafting using the same initial concentration (1.5 wt.% Zr/SiO$_2$).

According to Table 1, the consumption of silanol groups with PMHS reaction led to a significant reduction of resulting zirconocene species (ca. 60%). Similar behavior was also observed in the case of less sterically hindered organosilanes, such as Me$_3$SiCl and Me$_2$HSiCl, for instance [10].

The surface of the supported catalysts was monitored by DRIFTS [12]. This showed the presence of isolated hydroxyl groups on silica which have an OH stretching band at $3746 \, cm^{-1}$. This band decreases in intensity with the impregnation with PMHS and with the grafting of the catalyst. Preliminary experiments showed that for 8.0 wt.% Si/SiO$_2$, there are still isolated silanol groups present. We verified that when the metallocene is grafted onto silica impregnated over 3.0 wt.% PMHS/SiO$_2$, the band corresponding to isolated hydroxyls almost disappeared, showing that metallocene consumes all the remaining hydroxyl groups that did not react with PMHS (Fig. 1). However it is possible that the metallocene could also be grafted on the Si–H bonds of PMHS as it was already shown by the DRIFTS studies [12].

Ethylene homopolymerization and ethylene/1-hexene copolymerization were studied for the different (nBuCp)$_2$ZrCl$_2$/PMHS/SiO$_2$ systems. According to Fig. 2, in both

Scheme 1.

Fig. 1. DRIFTS spectra of (a) silica activated at 450 °C; (b) after chemical modification with 3.0 wt.% Si/SiO$_2$ of PMHS; (c) the same as in (b), followed by grafting (nBuCp)$_2$ZrCl$_2$ from toluene solution (0.3 wt.% Zr/SiO$_2$).

cases catalyst activity increases with the amount of PMHS on the support up to 5.0 wt.% Si/SiO$_2$, decreasing in the case of 8.0 wt.% Si/SiO$_2$. Comparing homo- and copolymerization for each supported system, no clear comonomer effect, i.e., higher catalyst activity in the case of copolymerization, could be observed. It is worth noting that copolymers are soluble in the polymerization medium facilitating the diffusion of the monomer to the catalyst sites.

The resulting polyethylenes were characterized in terms of their molecular weights (M_w), molecular weight distribution (M_w/M_n), melting temperature (T_m) and crystallization (χ_c). According to Table 2, all the resulting homopolymers have high molecular weights. In four systems, bimodal curves were observed, suggesting the possibility of existence of more than one active surface species. A typical GPC

chromatogram is shown in Fig. 3. Melting temperatures are higher for polymers produced by systems bearing 5.0 and 8.0 wt.% Si/SiO$_2$ indicating a more crystalline structure.

The properties of ethylene/1-hexene copolymers are presented in Table 3. Comparing M_w data from Table 3 with

Table 2
Molecular weights and distributions and thermal properties of the homopolymers of ethylene obtained with the system (nBuCp)$_2$ZrCl$_2$/PMHS/SiO$_2$

Catalyst (wt.% Si/SiO$_2$)	M_w ($\times 10^{-5}$)	M_w/M_n	T_m (°C)	χ_c (%)
0.15	160000	2.4	133	59
0.3	170000/8000	1.5/1.3	133	41
0.5	150000	2.3	126	39
1.0	210000	2.1	133	64
3.0	300000/17000	1.7/1.3	132	74
5.0	150000/8000	1.7/1.7	141	70
8.0	440000/21000	1.7/1.3	140	72

Table 3
Molecular weights and distributions and melting temperatures and crystallinities of ethylene/1-hexene copolymers obtained with the system (nBuCp)$_2$ZrCl$_2$/PMHS/SiO$_2$

Catalyst (wt.% Si/SiO$_2$)	M_w ($\times 10^{-5}$)	M_w/M_n	T_m (°C)	χ_c (%)	[H] (mol%)
0.15	126000	2.6	109	19	3.4
0.3	91000	2.8	107	23	3.6
0.5	99200	1.6	112	24	3.0
1.0	92400	4.9	106	23	3.5
3.0	55100	1.9	105	28	3.6
5.0	80000	1.6	106	23	3.4
8.0	61000/9000	1.1/1.5	107	25	3.2
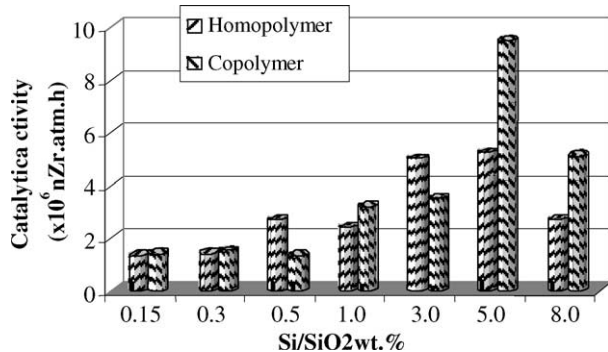
Fig. 2. Catalyst activity in ethylene homopolymerization and ethylene/1-hexene copolymerization of the supported systems on silica modified with PMHS.
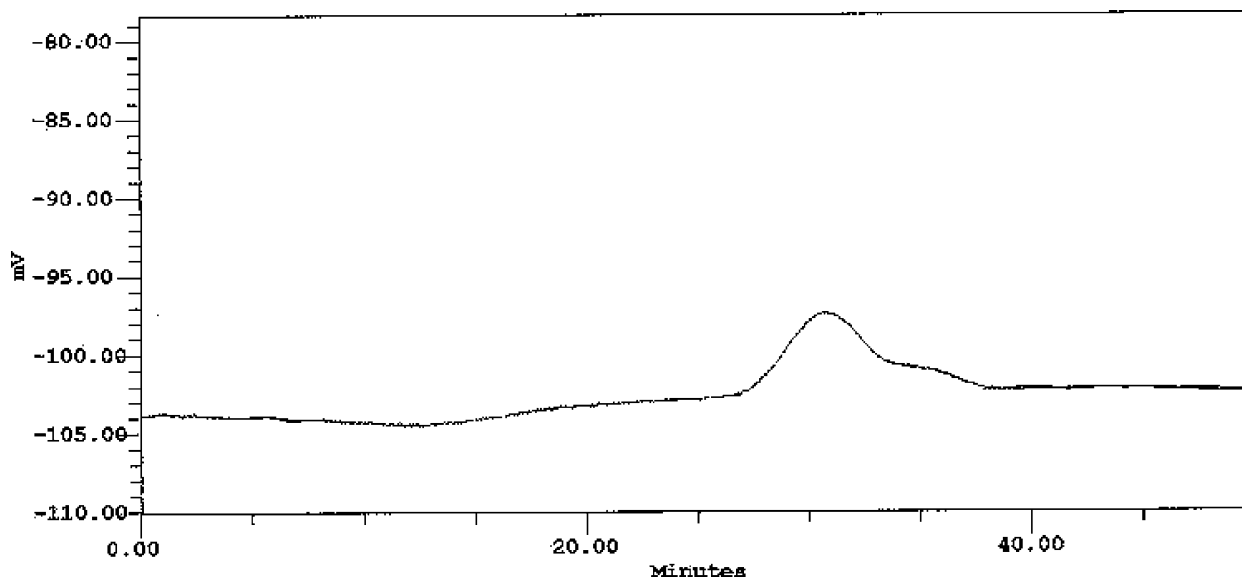
Fig. 3. GPC chromatogram of polyethylene obtained with $(nBuCp)_2ZrCl_2$/PMHS/SiO$_2$ (0.3 wt.% Si/SiO$_2$).

Table 2, we observe that copolymer M_w is lower than those of homopolymers. These results suggest chain transfer reaction to comonomer. Almost all of GPC curves are unimodal with the exception of the copolymer obtained with the system corresponding to 8.0 wt.% of Si/SiO$_2$ where two peaks can be observed as shown in Fig. 4. The unimodal chromatograms suggest that copolymerization reactions seem to take place preferentially on a specific type of site. In the case of the highest PMHS value (8.0 wt.%) on SiO$_2$, there might be the generation of a second catalyst site, probably though interaction with the polyorganosilane chain. Therefore, the resulting polymer is characterized by bimodal GPC curve, which traduces the likely presence of two different catalyst sites. These results suggest that upon grafting the zirconocene onto the PMHS-modified silica, two types of catalyst site are formed. Probably, one could be generated on residual silanol groups and a second formed by reaction of the Si–H bond from PMHS with the zirconocene.

1-Hexene incorporation in the resulting copolymers was studied by ^{13}C NMR. According to Table 3, increasing amounts of PMHS on silica surface do not influence the amount of 1-hexene incorporated, which remained roughly close to 3.4 mol%. The melting temperature and crystallinities are in agreement with the level of comonomer incorporation.
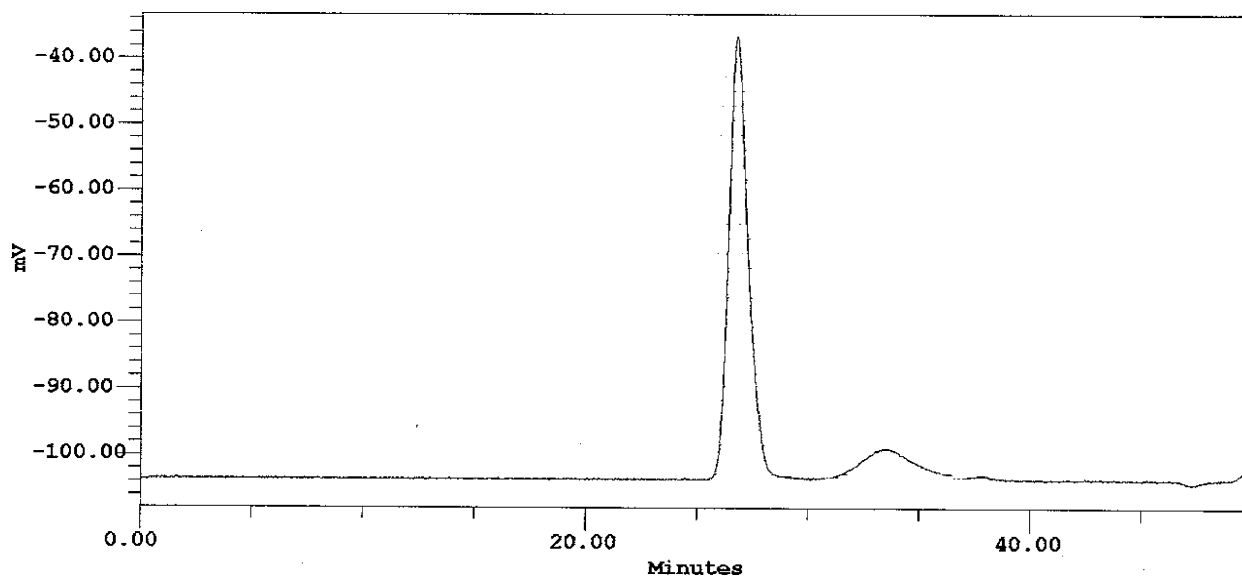
Fig. 4. GPC chromatogram of ethylene/1-hexene copolymer obtained with $(nBuCp)_2ZrCl_2$/PMHS/SiO$_2$ (8.0 wt.% Si/SiO$_2$).

Table 4

Triads, comonomers number average sequence length (n), and ethylene reactivity ratio (r_E), calculated by ^{13}C NMR, of the ethylene/1-hexene copolymers obtained with the system $(nBuCp)_2ZrCl_2/PMHS/SiO_2$

Catalyst (%Si)	[H] (mol%)	[HHH] (mol%)	[EHH] (mol%)	[EHE] (mol%)	[EEE] (mol%)	[HEH] (mol%)	[HEE] (mol%)	n_E	n_H	r_E
0.15	3.4	0	0	3.4	89.8	0	6.8	28	1.0	94.7
0.3	3.6	0	0	3.6	89.3	0	7.1	27	1.0	89.8
0.5	3.0	0	0	3.0	91.1	0	6.0	32	1.0	108.7
1.0	3.5	0	0	3.5	89.6	0	7.0	28	1.0	92.4
3.0	3.6	0	0	3.6	89.3	0	7.1	27	1.0	90.3
5.0	3.4	0	0	3.4	89.9	0	6.8	29	1.0	95.3
8.0	3.2	0	0	3.2	90.5	0	6.3	31	1.0	102.1

The microstructure of the copolymers was studied by ^{13}C NMR (Table 4). The absence of [HHH], [EHH] and [HEH] triads suggests random copolymerization. The comonomer average sequence lengths and ethylene reactivity ratios were calculated from the NMR data. Sequence length calculation showed that copolymers are formed by ca. 28–31 ethylene units between 1-hexene ones. Reactivity ratios remained roughly between 90 and 100.

The effect of chemical modification of silica with other compounds on the grafted content, catalyst activity and polymer properties was also investigated. Silica was modified with Me_3SiCl, Ph_3SiOH, $SnCl_4$, isodrin and aldrin. Fig. 5 shows catalyst activity exhibited for these different systems, while Tables 5 and 6 present the copolymer properties and microstructure characterization, respectively. For comparison, data for the homogenous catalyst and of $(nBuCp)_2ZrCl_2$ supported on bare silica were also included.

$(nBuCp)_2ZrCl_2$ was grafted on SiO_2 modified with Me_3SiCl bearing 0.3 and 1.0 wt.% Si/SiO_2. According to RBS measurements, the former led to 0.6 wt.% Zr/SiO_2, and the latter to 0.3 wt.% Zr/SiO_2. Silica modified with lower Me_3SiCl content probably has more residual silanol groups available to react with the metallocene. The resulting catalyst systems were also evaluated in ethylene homo- and copolymerization reactions. In the case of ethylene homopolymerization, an increase in catalyst activity was observed as the amount of Me_3Si groups increased on the silica surface: 1.3×10^6 and 2.0×10^6 gpol/(gmol
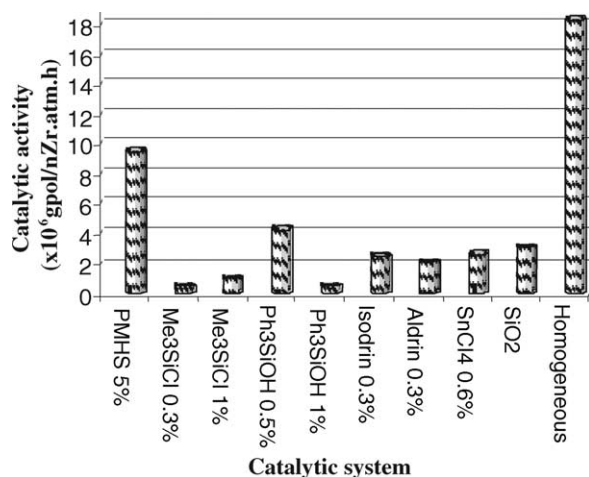

Fig. 5. Catalyst activity in ethylene/1-hexene copolymerization of homogeneous and supported systems on silica modified with different spacers.

Zr. bar h) for the systems with 0.3% and 1.0 wt.% Si/SiO_2, respectively. This can be attributed to the generation of more widely spaced catalyst species on the silica surface, reducing bimolecular deactivation reactions.

Similar behavior was observed in the case of ethylene/1-hexene copolymerization. Catalyst activity (Fig. 5) and comonomer incorporation (Table 5) were lower than that achieved in the case of PMHS-modified silica or even in the case of grafting on bare silica. The difficulties in

Table 5

Characteristics of the copolymers ethylene/1-hexene obtained with the system $(nBuCp)_2ZrCl_2/spacer/SiO_2$

Catalyst	Spacer/SiO₂ (wt.%)	[H] (mol%)	T_m (°C)	χ_c (%)	M_w (g/mol)	M_w/M_n
1	0.0	4.5	104	32	47200	2.5
1/SiO₂	0.0	3.6	108	30	130000	2.2
1/PMHS/SiO₂	5.0	3.4	106	23	80000	1.6
1/Me₃SiCl/SiO₂	0.3	1.8	113	35	120000	3.2
1/Me₃SiCl/SiO₂	1.0	2.0	114	27	98200	2.0
1/Ph₃SiOH/SiO₂	0.5	3.5	107	27	128500	2.0
1/Ph₃SiOH/SiO₂	1.0	3.1	111	36	75700	2.1
1/Isodrin/SiO₂	0.3	2.8	107	22	107800	1.9
1/Aldrin/SiO₂	0.3	2.6	110	23	110000	2.6
1/SnCl₄/SiO₂	0.6	3.7	108	22	158800	2.4

$1 = (nBuCp)_2ZrCl_2$.

Table 6
Triads, comonomers number average sequence length (n), and ethylene reactivity ratio (r_E), calculated by ^{13}C NMR, of the ethylene/1-hexene copolymers obtained with the system (nBuCp)$_2$ZrCl$_2$/spacer/SiO$_2$

Catalyst	[H] (mol%)	[HHH] (mol%)	[EHH] (mol%)	[EHE] (mol%)	[EEE] (mol%)	[HEH] (mol%)	[HEE] (mol%)	n_E	n_H	r_E
Me$_3$SiCl 0.3[a]	1.8	0	0	1.8	94.7	0	3.5	56	1.0	190.4
Me$_3$SiCl 1.0[a]	2.0	0	0	2.0	94.0	0	4.0	49	1.0	165.7
Ph$_3$SiOH 0.5[a]	3.5	0	0	3.5	89.6	0	6.9	28	1.0	92.8
Ph$_3$SiOH 1.0[a]	3.1	0	0	3.1	90.8	0	6.1	32	1.0	106.1
Isodrin	2.8	0	0	2.8	91.6	0	5.6	35	1.0	116.4
Aldrin	2.6	0	0	2.6	92.1	0	5.2	37	1.0	126.0
SnCl$_4$	3.7	0	0	3.7	89.0	0	7.3	26	1.0	87.2

[a] Expressed in terms of wt.% Si/SiO$_2$.

1-hexene incorporation are also evidenced by the high ethylene reactivity ratios ($r_E = 165.7$ and 190.4, Table 6) determined for this system. Triad distributions calculated from ^{13}C NMR data also indicate a random distribution of comonomer (Table 6). The molecular weight obtained with the supported catalyst with higher amount of Me$_3$SiCl is higher than that the obtained with the lower amount. For both systems, GPC curves were unimodal and narrow.

The effect of more sterically demanding ligands was evaluated by modifying the silica surface with Ph$_3$SiOH at two levels: 0.5 and 1.0 wt.% Si/SiO$_2$. Grafting (nBuCp)$_2$ZrCl$_2$ on the Ph$_3$SiOH-modified silicas resulted 0.4 wt.% Zr/SiO$_2$ in both cases, suggesting that grafted content may be determined by the steric effect of the ligands from the zirconocene itself which might prevent further reaction [20]. In the system prepared on the silica modified with 0.5 wt.% of Si/SiO$_2$, higher catalyst activity was observed relative to those using Me$_3$SiCl as modifier. We cannot neglect the possibility of a chemical effect played by the phenyl groups which seems to engender some positive effect in the case of 0.5 wt.% Si/SiO$_2$. The presence of phenyl groups on silica surface are well know to induce polarity in silica surface (as currently employed to alter phase polarity in chromatography science). Thus it seems that the phenyl groups might interact with the Zr catalyst center, tuning its cationic character. On the other hand, it is worth mentioning that much higher phenyl contents are deleterious, leading to a reduction in catalyst activity. Both systems have a higher 1-hexene incorporation (3.1–3.5 mol%) compared to those observed in the case of silica modified with Me$_3$SiCl, and are similar to those observed in the case of PMHS-modified systems. As in the case of Me$_3$SiCl, catalysts bearing higher spacer content produce copolymers with lower molecular weight. Copolymer polydispersity was around 2.0, indicating that zirconocene single-site nature was retained in these supported systems. According to Table 6, random distribution of comonomer was also observed and comonomer average sequence length and reactivity ratios were similar to those exhibited by PMHS-modified catalysts.

Silica was also modified with isodrin (0.3 wt.%), aldrin (0.3 wt.%) and SnCl$_4$ (0.6 wt.% Sn/SiO$_2$). The resulting grafted contents were 0.4, 0.4 and 0.3 wt.% Zr/SiO$_2$, re-

spectively. For the three systems, catalyst activity was very similar (see Fig. 5), but lower that observed in the case of PMHS-modified catalysts. Among these three systems, the tin-modified one afforded 3.7 mol% 1-hexene incorporation, exhibiting therefore the highest comonomer incorporation among the supported systems. In spite of this, copolymer produced with this catalyst systems had higher M_w in comparison to those obtained with organosilicon-modified silica. For these three systems, polydispersity ranged between 1.9 and 2.6. Triad distributions, comonomer average sequence lengths and ethylene reactivity ratios for these last systems are listed in Table 6.

According to Fig. 5, the homogeneous catalysts exhibited the highest catalyst activities. This is expected because in homogeneous systems, each molecule is potentially a catalyst center, while in the supported ones, not necessarily all the grafted metal content represents active and accessible catalyst sites. Besides, it seems that only 1% of grafted zirconocene is effectively active [21]. The reduction in activity in the case of supported systems is also explained by the steric effect played by silica surface, which acts as a huge ligand, hindering the access of the monomer to catalyst site. This effect of silica surface seems to be attenuated in the case of oligomeric PMHS, which might engender active zirconocene species far from the surface, being therefore more accessible. Similar results were reported in the case of organosilane spacers, in which an increase in catalyst activity in ethylene homopolymerization was also observed [22]. Most of the other chemical modifiers, which are less sterically demanding molecules in comparison to oligomeric PMHS, afforded supported systems with catalyst activity comparable to that observed for supported metallocene on bare silica. It is worth mentioning that in the case of ethylene homopolymerization, the use of some of these spacers led to an increase in catalyst activity, which was attributed to the role as *horizontal spacer*, hindering bimolecular deactivation reaction [10,11]. According to Fig. 5, such effect is not observed in the case of ethylene/1-hexene copolymerization, where roughly all the other supported systems exhibited comparable catalyst activity. It seems that the kinetics of 1-hexene incorporation might predominate over steric effects.

Comparing copolymers produced by homogeneous and supported catalysts (Table 5), we observe that the copolymer obtained with homogeneous $(nBuCp)_2ZrCl_2$ has lower M_w than those obtained with heterogeneous systems. This fact could be attributed to the blocking of one of the sides of the active site by the support, hindering the deactivation step. In other words, the β-elimination transfer reaction between two metallocene centers is hindered, resulting in a faster growth of the polymer chain, and therefore in a higher molecular weight [22].

For steric reasons, homogeneous catalysts also afford high comonomer incorporation (see Table 5). Nevertheless, no clear trend could be established among the supported catalysts. Copolymers obtained using zirconocene grafted on bare silica, as well as PMHS-, Ph_3SiOH- and $SnCl_4$-modified silica, led to comparable 1-hexene incorporation levels.

4. Conclusions

Grafting $(nBuCp)_2ZrCl_2$ on PMHS-modified silica afforded catalyst systems active in ethylene/1-hexene copolymerization in the presence of MAO as cocatalyst. The highest activity was achieved in the case of silica modification with PMHS (5.0 wt.% Si/SiO_2). Chemical modification with this spacer seems to generate two surface species, as indicated by the bimodality exhibited by PE in their GPC curves: one is probably produced by the reaction of metallocene with Si–OH from silica and another by the reaction of metallocene with Si–H from PMHS. Other studied spacers showed lower catalyst activity, in the following order: PMHS > Ph_3SiOH > bared SiO_2 > isodrin ∼ $SnCl_4$ > aldrin > Me_3SiCl.

PMHS proved to be an interesting molecule to use as spacer on silica surface affording supported zirconocene catalyst that is three times as active compared to that supported on bare silica. $(nBuCp)_2ZrCl_2$ supported on PMHS-modified silica exhibited catalyst activity which was the half of that of the homogeneous system, indicating a potential approach to increasing catalyst activity of supported metallocenes.

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