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Comparative study of propylene polymerization using $Me_2Si(RInd)_2ZrCl_2/SiO_2-SMAO/AlR_3$ and $Me_2Si(RInd)_2ZrCl_2/MAO$ (R = Me, H)

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Abstract

A mechanistic analysis of propylene polymerization was performed, in which the catalyst system was $Me_2Si(R^1Ind)_2ZrCl_2/SMAO/AlR^2_3$ (in situ supported catalyst onto MAO-modified silica) or $Me_2Si(R^1Ind)_2ZrCl_2/MAO$ (homogeneous), where $R^1 = H$ or CH_3, cocatalyzed by AlR^2_3 = TEA (triethylaluminum), IPRA (isoprenylaluminum), or TIBA (triisobutylaluminum). The catalyst activity of the homogeneous system $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2/MAO$ was almost 8 times higher than that observed for $Me_2Si(Ind)_2ZrCl_2/MAO$ (38 vs 4.6 kg PP/g cat h), while the polypropylene molar mass was 3 times higher (M_w: 93 vs 34 kg/mol). Conversely, the in situ supported systems $Me_2Si(Ind)_2ZrCl_2/SMAO/AlR_3$ and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2/SMAO/AlR_3$ showed similar activities, ranging from 0.2 to 1.5 kg PP/g cat h. The molar mass of the resulting polymers prepared using the in situ procedure was dependent on the AlR_3 nature and on the Al/Zr ratio. Generally, the heterogeneous catalysts produced PP with higher molecular weights than that obtained with homogeneous ones. The influence of the alkylaluminum, used as the cocatalyst, on the chain-transfer termination reaction to the alkyl compound was evident from the activity and the molecular weight of the produced polymers.

Keywords: In situ immobilization; Metallocene catalyst; Polypropylene

1. Introduction

The olefin polymerization catalysts based on metallocenes have been considered to function as a single active center catalyst. This fact is the explanation given to the high degree of molecular regularity of the polyolefins obtained with metallocenes, which in turn is reflected by a relatively low dispersity index and by a lack of long chain branching [1]. For gas-phase and slurry processes, however, soluble metallocene catalysts have to be immobilized, usually by supporting them on a suitable carrier. The goal is that the immobilized metallocene retains the essential characteristics of its homogeneous analogues. Several routes of heterogenization have been proposed in the literature [2] involving, for instance, direct immobilization on silica or on chemically modified supports just to mention a few. These protocols contain several steps, which make them time demanding.

The in situ metallocene catalyst immobilization on SiO_2 support was first used by Soares et al. in homo- and copolymerization of ethylene [3–9]. The optimization of such systems in terms of the MAO amount and of the kind of alkylaluminum, employed as the cocatalyst, has not been reported

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in detail. More recently, Lee et al. employed the same procedure with a newly synthesized pentamethylene bridged dinuclear zirconocene catalyst, also in ethylene homo- and copolymerization [10]. In all the above-mentioned works, the polymers showed a well-defined morphology and replicated the support, confirming that the catalyst was immobilized onto the silica surface and was not present in the solution at detectable levels or in an active form.

The comparison between the 2-alkyl substituted indenyl compounds with their unsubstantiated analogues under homogeneous conditions is not new [11,12]. Soga et al. [11] studied the homogeneous polymerization of propene using C_2 symmetrical zirconocenes *rac*-Et (2,4,7-Me3Ind)$_2$ZrCl$_2$, and *rac*-Me$_2$Si(2-Me4-PhInd)$_2$ZrCl$_2$ combined with MAO or Ph$_3$CB(C$_6$F$_5$)$_4$. The isotacticity and the melting point of the produced polymers increased markedly in comparison with the non-substituted analogues, while exhibiting a decrease in the polymerization temperature from 30 to −78 °C. Waymouth's group [12–14] studied the homogeneous polymerization of propylene to elastomeric polypropylene using 2-arylindenylzirconocenes.

Brintzinger et al. [15] and Spaleck et al. [16] have discovered that the substitution on the second and fourth positions of silylene bridged bis-indenylzirconocenes leads to catalysts that afford higher polypropylene (PP) molecular weight with higher yields. When position 2 was substituted by a methyl, productivity of Me$_2$Si(2-MeInd)$_2$ZrCl$_2$ was nearly the same as that observed for EtInd$_2$ZrCl$_2$, but the molecular weight of PP was roughly 8 times higher (195,000 vs 24,000 Da). When the position 4 of indenyl was also substituted by isopropyl group, the activity increased nearly 25% and the molecular weight of the obtained PP was slightly higher (213,000 Da) than that determined in the catalyst system bearing only the 2 methyl substitution.

In combination with MAO, *rac*-Et(*tert*-butyldimethylsiloxiInd)$_2$ZrCl$_2$ polymerizes propylene to highly a isotactic polymer of $T_m = 148$ C and $M_w = 45{,}600$ in homogeneous phase [17]. It seems that the substitution in position 2 is related to an increase in the molecular weight.

The in situ procedure implies that the MAO-modified silica (SMAO) is separately added to the zirconocene within the reactor. The supporting reaction takes place in parallel to the polymerization itself in the presence of the monomer. In our previous publications [18–20], it was shown that this procedure could be also used to polymerize propylene using the catalysts Me$_2$Si(Ind)$_2$ZrCl$_2$ and Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$, with common alkylaluminums as the cocatalysts and the commercial SMAO as the support. It is known that the use of alkylaluminums in the soluble systems decreases the activity of the catalyst. The alkylaluminum nature and concentration had influence on the catalyst activity, on the polymer properties and on the number and behavior of each active center [21]. Some of us have published several manuscripts dealing with the use of immobilized zirconocenes and different cocatalysts, mainly MAO and alkylaluminums. In our previous work, no metallocene leaching from the support to the solution was found to take place when SMAO was used as the support in the in situ method. The resulting polymers in the case of the in situ procedure were different from those obtained with the homogeneous system [18–20]. Besides, SEM micrographs of the polymers confirmed that the polymerization took place on the catalyst grain [22].

Considering the theoretical aspects, the modern quantum mechanics and/or the molecular mechanics can adequately model several steps of the polymerization reactions by metallocene catalysts. In many cases, the results provide valuable preliminary information to design experimental work to be developed with new catalyst systems.

Comparison of Molecular Mechanics (MM) calculations to Density Function Theory (Dmol-MSI) in the evaluation of the most stable structures of a selected catalyst (Cp$_2$ZrCH$_3^+$) and a borane cocatalyst ([B(Ph)$_4$]$^-$ has been recently published. Bond length and angles slightly differed from the results calculated by both methods [23]. The potential energies were almost identical. The results suggested that the MM2 calculation could evaluate the interaction strength between the atoms in these systems very well. By using MM calculations, the most stable structures of the catalyst–cocatalyst systems were calculated, which have faced serious difficulties by Molecular Orbital calculations due to the heavy load of too many atoms. The energy of interaction between the catalyst and the cocatalyst was also calculated, among several other structural parameters. Based on the quantitative relationship between the catalyst activities and these factors using the QSAR analysis, the structural factors related to the distance between the metal center on the catalyst and the cocatalyst were found to be very effective. The authors concluded that the activity of the metallocene depends on the chemical structures of the catalyst, the cocatalyst and the monomer. They also proposed that the activity could be roughly estimated by molecular mechanics and molecular dynamics calculations, without the necessity of using demanding techniques such ab initio molecular orbital calculations. QSAR analysis has been applied several times in metallocene chemistry with good estimations for ethylene and propylene polymerizations. Several manuscripts have been published on the use of the force fields to predict the geometries of several substituted and ring-bridged zirconocene complexes [24–26].

The first attempt in correlating experimental data, such as the polymerization activity and the polymer molecular weight, with the 3D structural properties of the catalyst active species was published in 2004 [27]. Differences in the polymerization activity data could be explained in terms of the steric and electronic fields.

In the present investigation, the results of activity and stereoselectivity in propylene polymerization performed with the in situ supported Me$_2$Si(Ind)$_2$ZrCl$_2$ and Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$ catalysts were comparatively investigated from a mechanistic point of view. It aimed at providing an explanation of the properties of the resulting polypropylene and of the catalysts' activities. Using a localized MM2 calculation, the step of propylene coordination in the models of supported catalysts and its potential role in the stereospecificity and the regioregularity of the products were studied for the substituted and the non-substituted zirconocene. Propylene coordination was considered *re* or *si* (primary and secondary) and the first two insertions were analyzed.

2. Experimental

2.1. Materials

All the experiments were performed under inert atmosphere using Schlenk techniques. The catalysts *rac*-dimethylsilylenebis(indenyl)zirconium dichloride ($Me_2Si(Ind)_2ZrCl_2$) (Crompton) and *rac*-dimethylsilylenebis(2-methyl-indenyl)zirconium dichloride ($Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$) (Boulder Scientific), the MAO-modified silica (SMAO, 23 wt.% Al, Crompton), and the cocatalysts MAO (10 wt.% in toluene, Crompton), triethylaluminum (TEA), isoprenylaluminum (IPRA), and triisobutylaluminum (TIBA) (all from Akzo) were used without purification. Propylene was used as received from the cracker (Copesul, Triunfo, RS, Brazil), without any further purification. Toluene and hexane were purified by refluxing over sodium followed by distillation. Hexane was degassed by bubbling nitrogen before each reaction.

2.2. Polymerization

Polymerizations were done in a 1.5-L stainless steel reactor equipped with a mechanical stirrer, a constant temperature circulator, and inlets for nitrogen and propylene. The reactor was filled with SMAO ($Al_{SMAO}/Zr = 500$ (mol/mol)), 0.75 L of hexane, 10 mL of catalyst solution (10^{-5} mol of the catalyst in toluene), and alkylaluminum. When the mixture reached 60 °C, the stirring rate was set at 750 rpm and the reactor was pressurized with propylene up to 6.0 bar (partial pressure) for 60 min. Acidified ethanol was used to quench the process. The product was filtered, washed with distilled water, washed with ethanol, and dried at 80 °C under vacuum. The mass of the dry polymer was weighed to determine the product yield. Each polymerization reaction was repeated at least twice, the variation being kept below 10%. All the results presented in this paper are the average of these values. The homogeneous polymerizations were carried out in the same way, but only MAO ($Al_{MAO}/Zr = 500$) was added into the reactor with the catalyst.

2.3. Polymer characterization

Melting temperatures (T_ms) were determined using a TA Instruments 2920 differential scanning calorimeter (DSC), according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan are reported here. The heating rate was 10 °C/min in the temperature range from 30 to 200 °C, and the analysis was done under a nitrogen atmosphere. Molar mass distributions were determined by high-temperature gel permeation chromatography (GPC) using a 150C Waters instrument equipped with four columns GMHXL-HT (TosoHaas) at 138 °C. 1,2,4-Trichlorobenzene was used as the mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards. Polypropylene microstructure was determined by ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy. ^{13}C NMR spectra were obtained at 120 °C in a Varian Inova 300 equipment operating at 75.4 MHz. Sample solution of the polymers was prepared in a *o*-dichlorobenzene (ODCB) and tetrachloroethane TCE-d_2 in 10 mm sample tubes. Spectra were taken with an acquisition time of 1.8 s and a delay of 10.0 s.

2.4. Theoretical methods

The active site of the metallocene is a cationic, alkylated, organometallic complex with the cocatalyst, carrying a vacant coordination site where the polymerization takes place. The calculations are based on the cationic species. In the present case, a particular structure for MAO was selected, taking into account experimental and theoretical approaches. In the manuscript of Cruz et al. [27], the steric field was considered a suitable 3D tool to explain differences in activity and molecular weight data, which is the aim of the present study. In Ref. [27], the cocatalyst was not explicitly considered. We tried to improve the approach and included the Zurek and Ziegler [28] proposition of the MAO structure in our model.

The steric energy is presented as the integration of bond stretching, bond-angle bending, torsion angle in deformations and non-bonded interaction energies along with other relevant terms. It is an empirical number that does not account for electronic interactions, even when it can provide approximate ion–ion interactions and dipole–dipole interactions. Only different conformations with the same atom number and different atom distributions – with no broken bonds, but conformationally different – can be compared, using the same force field and the same number and kind of bonds involved. However, there are several publications about the use of molecular mechanics in the study of steric interactions, even in transition metal complexes [27–30].

The MM2 analysis of the catalyst, the cocatalyst and the support structures was done using Chem3D Ultra 5.0 (from Cambridge Soft). MM2 from Chem3D (Cambridge Soft) was used as a tool to analyze the steric interactions between the MAO, the alkylaluminums, the zirconocene and the propylene with the methyl or with the growing chain (after the first insertion). The zirconium was modeled as a +1 cation, being the tetrahedral Al with −1 charge. All the parameters are included in the software package. The interactions were analyzed following the models of Zurek and Ziegler [28] and Ferreira [31].

3. Results

3.1. Polymerization activity and polymer characterization – comparison of experimental polymer properties produced by Catalyst 1 and Catalyst 2

Some of us published several manuscripts about the preparation and characterization of in situ supported metallocene

Table 1
Catalytic activity of the systems $Me_2Si(Ind)_2ZrCl_2$ (Cat1)/SMAO and $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ (Cat2)/SMAO in the presence of TEA, TIBA or IPRA and properties of the polymers obtained with homogeneous and in situ polymerization

Alkylaluminum		Activity (kg PP/g cat h)	T_m (°C)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
Type	Concentration (mol/mol)[a]					
$Me_2Si(Ind)_2ZrCl_2$–Catalyst 1 – Cat1						
Homogeneous polymerization[b]		4.6	142	16	34	2.1
TEA	100	0.4	141	21	45	2.1
	250	0.3	141	20	42	2.1
	500	0.3	140	16	30	1.9
TIBA	100	0.5	140	26	58	2.2
	250	0.6	141	30	63	2.1
	500	0.2	140	33	68	2.1
IPRA	100	1.4	141	21	45	2.1
	250	0.1	nd	nd	nd	nd
	500	0.2	139	28	61	2.2
$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$–Catalyst 2 – Cat2						
Homogeneous polymerization[b]		38	147	48	93	1.9
TEA	100	1.0	134[c]/145	69	128	1.9
	250	0.1	127[c]/142	33	61	1.9
	500	0.1	134[c]/145	17	50	2.9
TIBA	100	0.3	132[c]/146	56	116	2.1
	250	0.3	137[c]/145	67	131	2.0
	500	0.3	131[c]/146	102	255	2.5
IPRA	100	1.5	135[c]/142	52	123	2.4
	250	0.3	128[c]/143	100	218	2.2
	500	0.2	128[c]/143	155	247	1.6

nd: not determined.

[a] $Al_{alkylaluminum}/Zr$ ratio.

[b] $Al_{MAO}/Zr = 500$ mol/mol. Without external alkylaluminum.

[c] Small shoulder in the melting endotherms of the polymers.

catalysts [20–22,32]. $Me_2Si(Ind)_2ZrCl_2$ (Catalyst 1 – Cat1) presents lower activity than $Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ (Catalyst 2 – Cat2) (4.6 vs 38 kg PP/g cat h) in the homogeneous polymerization of propylene (see Table 1). The molar mass of the polymer produced by soluble Cat2 is 3 times higher than that obtained with soluble Cat1. In the case of the in situ supported catalyst, in which the alkylaluminum cocatalysts were used, the activity decreased, with a similar productivity level as for both supported Cat1 and Cat2, ranging from 0.1 to 1.5 kg PP/g cat h. In the case of Cat1, the soluble and supported catalyst generated a polymer with the same melting point, which suggests that they have similar microstructures.

As shown in Table 1, in the case of the substituted one (Cat2), the supported catalyst produces two groups of polymers: one with a higher amount of irregularities than that produced with the soluble catalyst and a second type, similar to that obtained with the soluble Cat2. Besides, a fraction of the polymers obtained with supported Cat2 showed higher melting points than those obtained with supported Cat1 (near 142–147 °C vs 139–142 °C). Supported Cat2 generated another fraction of polymer with a lower melting point (127–137 °C). One cannot discriminate if there is a lower amount of active sites with the same propagation constant or a different number of active sites, distinguished from the homogeneous one, with another propagation constant (the most probable).

3.1.1. *Cat1: effect of the nature of cocatalyst and the Al/Zr molar ratio on the activity and polymer properties*

In this case, using MAO at Al/Zr = 500, the activity is the highest among all the evaluated cases for Cat1 (4.6 kg PP/g cat h). A slight detrimental effect of the Al/Zr molar ratio is found in the supported catalysts using TEA (from 0.4 to 0.3 kg PP/g cat h) when 100–500 is used. This effect is much stronger in the case of TIBA (near the same activity with Al/Zr = 100 and 250 and much lower in the case of Al/Zr = 500). When IPRA is used, the highest activity is found for Al/Zr = 100 (ca. 1.4 kg PP/g cat h). It seems that a higher number of active sites is achieved here than in the case of using TEA at the same molar ratio (100). The polymer characteristics are the same using IPRA or TEA, although the activity is 3 times higher in the first case (1.4 kg PP/g cat h vs 0.4 kg PP/g cat h).

Increasing the amount of IPRA to 250–500 decreased the activity in one order of magnitude (0.1–0.2 kg PP/g cat h). Melting temperatures (T_ms) lay from 139 to 142 °C. There is only one peak in the DSC in all cases. Polydispersity ranged from 1.9 to 2.2 and no changes are aroused in the DSC in terms of number of peaks. Molecular weight distributions of polyolefins produced by homogeneous metallocenes are usually narrow, near 2. Some researchers have taken this as the criteria of a single site. In fact, this just means that the polymers are produced by one kind (or several) of catalytic species having a certain ratio of the rate constant of propagation to the rate constant of chain transfer. For instance the iPP produced by *rac*-EtInd$_2$ZrCl$_2$/MAO has the most probable polydispersity of 2. When the polymers were separated in several fractions according to solubility, each fraction has also a polydispersity of 2, although they differed in microstructures. Each fraction is produced by catalytic species with their own propagation and termination constants, but with a generally similar ratio of the propagation to termination constants. The displacement of the equilibrium between these species with temperature, zirconocene and propylene concentration contributes to changes in polyolefin structures [33].

T_m seems to be lower in the case of the supported Cat1, but molar mass is higher at several Al$_{alkylaluminum}$/Zr molar ratios (34 kg/mol for the soluble catalyst vs 30–68 kg/mol for the supported catalyst). In the case of TEA, increasing the Al/Zr molar ratio from 100 to 500 decreases the molar mass (from 45 to 30 kg/mol) (see Table 1). With TIBA at low Al/Zr molar ratios, the molar mass achieves 58 kg/mol, and the trend shows that increasing the Al/Zr molar ratio increases the molar mass (up to 68 kg/mol). When IPRA is used, the same general trend is found, but the molar mass of the polymer, obtained at Al/Zr = 100, is the same as that obtained using TEA (45 kg/mol). Using IPRA at an Al/Zr molar ratio of 500, the molar mass of the resulting polypropylene increases to 61 kg/mol. These results suggest that there is a different trend for TEA in the molar mass change in comparison to that observed for IPRA and TIBA, depending on the Al/Zr molar ratio.

3.1.2. Cat2: effect of the nature of cocatalyst and the Al/Zr molar ratio on the activity and polymer properties

In this case, using MAO at Al/Zr = 500, once again the activity is the highest among all the evaluated cases. A strong detrimental effect of the Al/Zr molar ratio on activity is found using TEA (from 1.0 to 0.1) when the Al/Zr molar ratio varies from 100 to 500. There is no effect in the case of TIBA (near the same activity in all range, from 100 to 500). When IPRA is used, the highest activity is found for Al/Zr = 100. It is evident that this activity is even higher than when using TEA at the same low molar ratio (1.5 vs 1.0 kg PP/g cat h). However, increasing the amount of IPRA to 250–500 decreased the activity one order of magnitude (to 0.2–0.3 kg PP/g cat h).

Polymers produced with the in situ supported catalyst show a second peak in the DSC thermogram at lower temperatures. Fig. 1 shows the endotherms of the polymers obtained with supported Cat1 and Cat2 using TEA at Al/Zr = 100. There is a neat shoulder in the 127–135 °C range in the polymer obtained with supported Cat2. Changes in the molecular weight of polypropylene are difficult to analyze in this case because it is clear that two different polymers have been produced. This fact is slightly reflected in the polydispersity (between 1.6 and 2.5 instead of near 2.1). Considering TEA as the cocatalyst, the trend is the same as in the case of supported Cat1: increasing the Al/Zr molar ratio decreases the molar mass of the produced polymer (from 128 to 50 kg/mol). In the case of IPRA and TIBA, once again the molar mass of the polypropylene increases as the Al/Zr molar ratio is increased from 100 to 500. The molar mass of the polymer produced at Al/Zr = 500 is in the same range as in this case (247–255 kg/mol) and it is twice as high as those obtained at Al/Zr molar ratio of 100 (116–123 kg/mol).

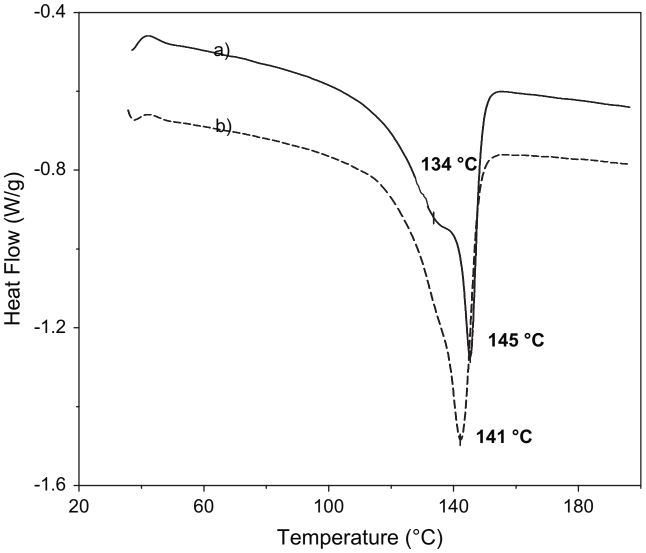


Fig. 1. Melting endotherms of the polymers produced in the presence of TEA (Al/Zr = 100) and SMAO with (a) Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$ and (b) Me$_2$Si(Ind)$_2$ZrCl$_2$.

3.2. The catalyst and cocatalysts model

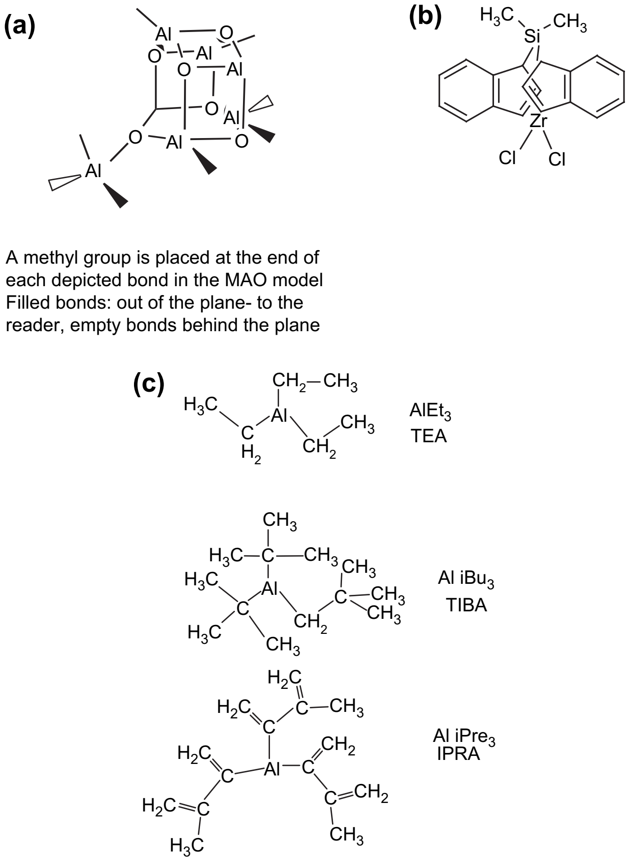
Fig. 2 shows the MAO model (including a TMA molecule), according to Zurek and Ziegler [28], and the zirconocene and the alkylaluminum models used in the calculations. The Zurek and Ziegler model took into account a lot of experimental references. The zirconocene was modeled with or without the methyl group in position 2 of the Cp. The aim of the MM2 calculation performed here was to understand the effect of the methyl group in position 2 of the Cp ring of the zirconocene related to the coordination of the incoming propylene (primary vs secondary and *si* vs *re*) in the simplified models of the supported systems, with no coordinated alkylaluminum. The importance of constraints in the coordination of propylene (and therefore local hindering to monomer coordination) can be related to the actual structure of the obtained polymer.

3.3. The generation of the active catalyst

The active sites in Cat1 and Cat2 are produced in several steps after the first contact with MAO. Depending on the form of this MAO (neat MAO or supported as in the case of SMAO), the metallocene is acting as a soluble or as an immobilized catalyst.

The mechanism of active site formation is considered as follows:

(1) Alkylation of the zirconocene and exchange of methyl by chlorine. This step can take place once or twice, generating R$_2$ZrClCH$_3$ and R$_2$Zr(CH$_3$)$_2$ [28].



A methyl group is placed at the end of each depicted bond in the MAO model
Filled bonds: out of the plane- to the reader, empty bonds behind the plane

Fig. 2. Structures of: (a) MAO with TMA (Zurek and Ziegler model); (b) $Me_2Si(Ind)_2ZrCl_2$; (c) alkylaluminum.

$$R_2ZrCl_2 + CH_3{-}SMAO \rightarrow R_2ZrClCH_3 + Cl{-}SMAO \quad (1)$$

$$R_2ZrClCH_3 + CH_3{-}SMAO \rightarrow R_2Zr(CH_3)_2 + Cl{-}SMAO \quad (2)$$

(2) Contact with SMAO and formation of the Zr-bridged methyl (chloride)–Al bond (or Zr–CH_3(Cl)–Al). NMR studies have demonstrated that chlorine is a suitable ligand to remain, especially in bulky structures like those considered here [1,2]. The bridge can be a methyl group (if double alkylation took place) or a chlorine atom (if single alkylation occurred). Other authors supported the formation of an inactive Zr–CH_2–Al bond [28]. The MAO model considered to be suitable is that from the modeling from Zurek and Ziegler [28], obtained by minimization of several proposed structures using DFT. The key role of the counter ion (MAO and MAO*TMA) has been recently studied using in situ FTIR and quantum chemical studies [34,35] suggesting that chlorine/methyl can be a bridge between MAO and the zirconocene on the active site.

$$R_2ZrClCH_3 + CH_3SMAO \rightarrow R_2Zr^+CH_3::Cl^-CH_3SMAO \quad (3)$$

$$R_2Zr(CH_3)_2 + CH_3SMAO \rightarrow R_2Zr^+CH_3::CH_3^-CH_3SMAO \quad (4)$$

Zurek and Ziegler [28] demonstrated that the coordination of Zr to an O from the MAO does not produce an active site, but a dormant one able to be reactivated by redistribution of ligands. The formation of a bond Zr-bridge (methyl or chlorine)–Al is a known step in the active site formation ([28] and references therein).

In the case of the SMAO, a step of CH_4 loss and formation of inactive Al–CH_2–Zr is proposed to take place at the immobilization step. A mechanism of supporting is proposed on MAO, where a surface reaction through Zr–CH_2–Al formation is considered as operative [36]. Some of us published papers about the quantification of methane evolved when the dichloride zirconocenes are fixed on MAO/SiO_2 [37]. The reaction implies the formation of a Zr–CH_2–Al bond.

$$R_2Zr^+CH_3::CH_3^-CH_3SMAO \rightarrow R_2Zr^+CH_3CH_2SMAO + CH_4 \quad (5)$$

$$R_2Zr^+Cl::CH_3^-CH_3SMAO \rightarrow R_2Zr^+ClCH_2SMAO + CH_4 \quad (6)$$

These species are considered to be inactive. The role of the alkylaluminum has been proposed and demonstrated to be involved in the realkylation of the zirconocene [38].

(3) Ion pair formation (tight), including different bridges and different ligand distributions (Zr tetrahedral in all cases) with the alkylaluminum as the alkylating agent.

$$R_2Zr^+CH_3CH_2SMAO + AlR_3 \rightarrow R_2Zr^+CH_3CH_2RAlR_2SMAO \quad (7)$$

$$R_2Zr^+ClCH_2SMAO + AlR_3 \rightarrow R_2Zr^+ClCH_2AlR_3SMAO \quad (8)$$

(4) First coordination of an olefin (propylene in this case) in a non-productive way, or a second molecule of alkylaluminum or a solvent molecule (toluene) (Zr pyramidal).

$$R_2Zr^+CH_2AlR_3ClSMAO + CH_3{-}CH{=}CH_2 \rightarrow R_2Zr^+{-}CH{=}CH_2CH_3::Cl^-CH_2SMA_O \quad (9)$$

$$R_2Zr^+CH_2AlR_3ClSMAO + AlR_3 \rightarrow R_2Zr^+RAlR_2CH_3::Cl^-CH_2SMAO \quad (10)$$

$$R_2Zr + CH_2AlR_3ClSMAO + C_7H_8 \rightarrow R_2Zr^+C_7H_8CH_3::Cl^-CH_2SMAO \quad (11)$$

(5) Ion pair separation (considering the effect of solvent plus olefin coordination) and propagative species formation. Olefin separated ion pairs are considered the active propagating sites in soluble and supported metallocene systems.

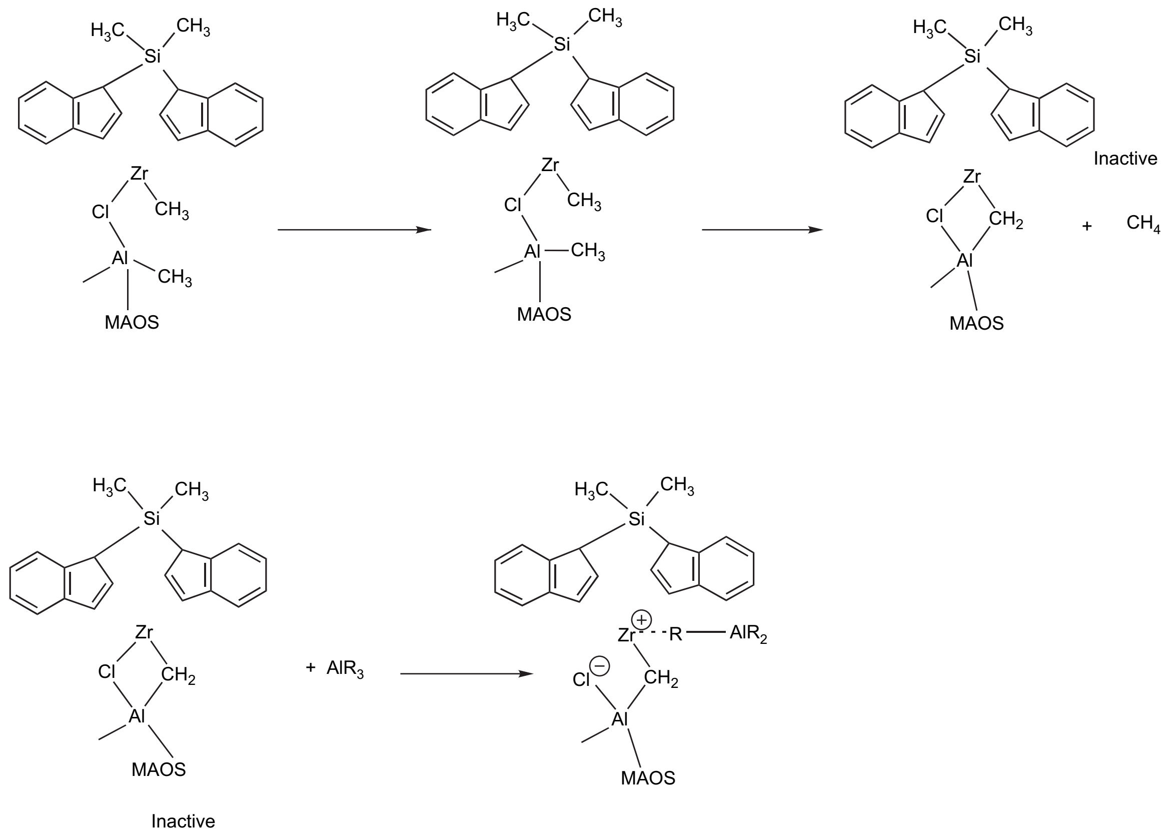


Fig. 3. Model of inactive species on SMAO and reaction with AlR_3 (Zr bonds to Cp centroids not included for the sake of clarity).

The coordination of zirconium on the active catalyst as a tetrahedral is an idea that is considered to be outdated today. Pentacoordination (and possibly hexacoordination if one takes into account the counter ion) is considered to be more realistic and, as shown by Ziegler group calculations, more related to the actual metallocenes' active sites [28]. Other authors [39,40] proposed a low energy intermediate as the contact ion pair with the direct coordination of the anion to the Zr center, and the presence of two different monomer molecules coordinated on the active site (but only one able to be polymerized). There are several recent works in the literature proposing metallocenes bearing high coordination metal centers [28,40–42]. The olefin separated ion pairs have been constantly considered and discussed for the last 10 years since the proposition by the Fusco group [43–45].

4. Discussion

According to Table 1, the activity of Cat1 and Cat2 decreases when SMAO is used with an alkylaluminum as the cocatalyst (heterogeneous) instead of MAO (homogeneous). From the results, one can postulate that there is in the in situ catalysts a kind of supported active site that is soluble-like and another effectively supported on SMAO, with a different structure than the "soluble-like". These supported active sites are very similar in the propagation to termination constant ratio in the case of Cat1 and are different in the case of Cat2. Previous studies allow us to consider that no leaching has taken place from SMAO in the case of supported Cat1 or supported Cat2 [38–40]. The alkylaluminums strongly affect activity.

(1) The active zirconocene is supported on SMAO and is not present in the solution. The interaction of the zirconocene with SMAO produces inactive Zr–CH_2–Al bonds. Alkylaluminums function as the realkylating agents.
(2) Cat2 generates different active sites on SMAO, whereas Cat1 is more homogeneous. In all the cases, one of the sides of the metallocene is blocked by the surface.
(3) The alkylaluminums affect the activity and the resulting molecular weight of the polymers.
(4) The effect of the alkylaluminum seems to be of steric and electronic nature.

4.1. Models for the active site structures for soluble and supported Cat1 and Cat2

Taking into account the ideas from Ferreira [31] and from the Brintzinger group [26,36–40] the inactive species of the zirconocene on SMAO are presented in Fig. 3. Fig. 4 shows the proposed structures for the active site when the zirconocenes are supported on SMAO, alkylaluminum is present

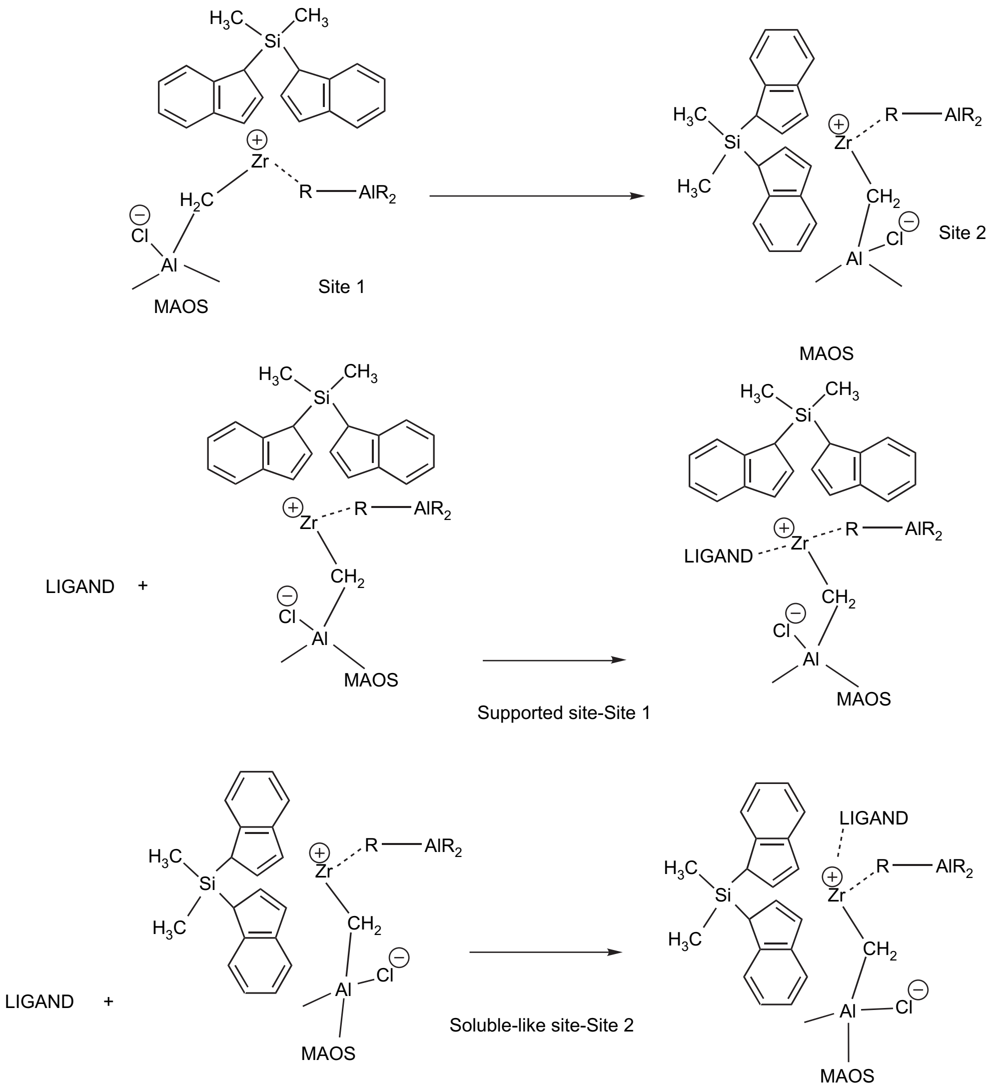


Fig. 4. Coordination of a non-polymerizable ligand (olefin, AlR_3). Zr bonds to Cp centroids not included for the sake of clarity.

and a further ligand completes the coordination of Zr. The main difference between one and the other is the distribution of ligands around the Zr (considering also the support as an additional ligand). The bridge between Zr and MAO is considered to be a methylene group or a Cl, following recent ideas published by Zurek and Ziegler [28]. Considering reported molecular modeling data on the structure of MAO and the interaction with the zirconocene (Ferreira [31]), this methyl group could have originated from the exchange of chlorine by methyl, whereas the methylene can be related to the reaction of 2 methyl groups to evolve methane. Therefore, one of the ligands of the MAO surface must be a chloride. The initial structure of this MAO is similar to that from the manuscripts of Barron et al. [41]. The supported MAO is not enough to activate metallocene and to generate the propagative species: the formation of the $Zr{-}CH_2{-}Al$ species renders inactive the supported SMAO.

The alkyl group on the zirconium can be initially provided by the supported MAO (and therefore it is methyl) or by the alkylaluminum (in this case it can be ethyl, isoprenyl or isobutyl) (see Fig. 5) [32]. The only configuration that allows this site to polymerize is to consider the change from penta- to hexacoordination upon coordination of a propylene molecule. There is no room for a second olefin to coordinate on the polymerization site. The single olefin is coordinated side by side to the alkyl group where it must be inserted. The location of the methyl group of the olefin must be analyzed with care because the ‘‘stereoregularity’’ of the insertion changes with the steric restrictions to coordination.

Fig. 6a and b shows the position of a coordinated olefin when the olefin separated ion pairs are considered to be formed on the two supported metallocenes. The effect of the alkylaluminum in the in situ supported catalyst is multiple. It can be coordinated to the bridged chlorine or be the alkyl donor to generate the first Zr–C bond and it can be a ligand coordinated to MAO, changing its properties on the surface. This effect can be better understood if we suppose that the alkylaluminum remains in the neighborhood of the cationic zirconocene, coordinated to the alkyl group, in the sense of Heinrici–Olive or Rodríguez and van Looy [42].

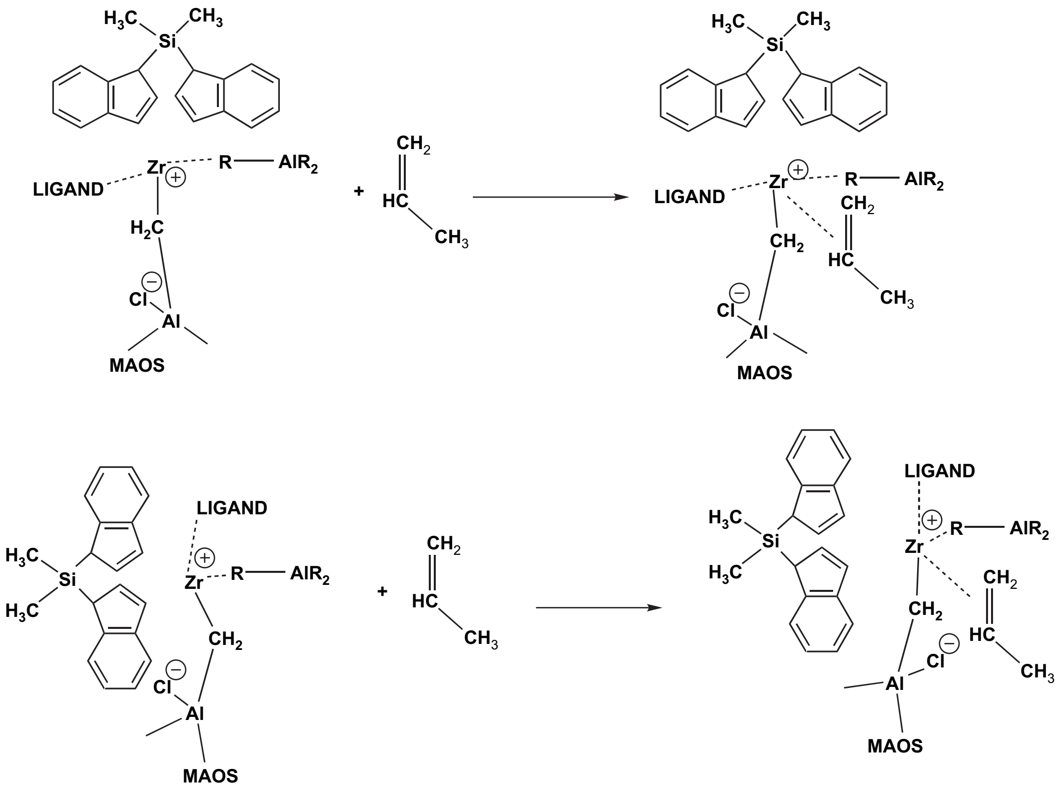


Fig. 5. Coordination of a polymerizable olefin – Zr bonds to Cp centroids not included for the sake of clarity.

Without the methyl group at position 2 of the Cp ring in the model presented in Fig. 4, one side presents Cp and the other presents Ph to the incoming propylene. The growing chain and the propylene site coordination can exchange places easily, and there is no hindrance. With a methyl at position 2, the situation changes (Figs. 6 and 7). Different propylene/growing

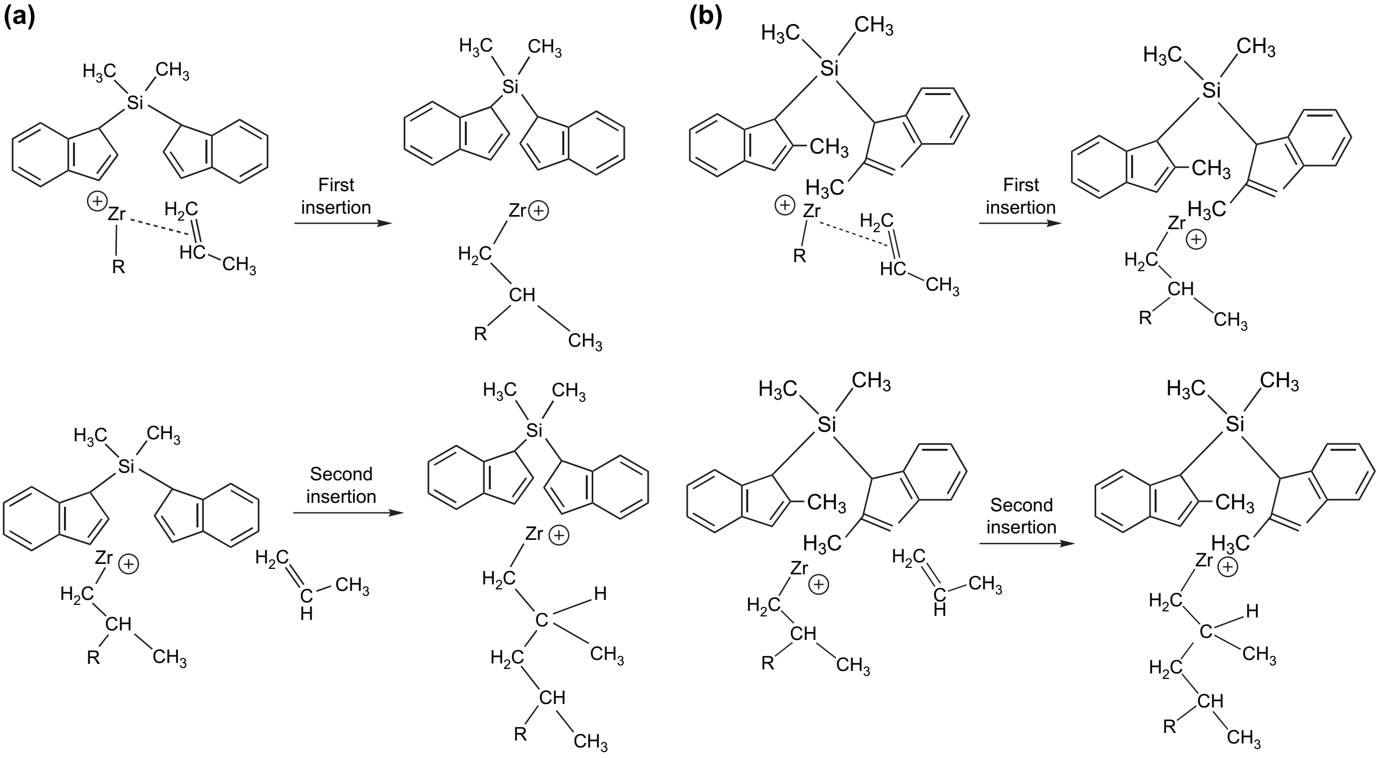


Fig. 6. (a) Role of H substitution in Cp in regio-/stereoselectivity of insertion – Cat1 – Zr bonds to Cp centroids not included for clarity. (b) Role of methyl substitution in regio-/stereoselectivity of insertion – Cat2 – Zr bonds to Cp centroids not included for clarity.

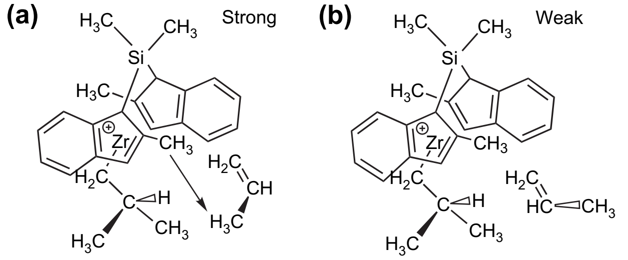


Fig. 7. (a) Interaction of methyl group in position 2 with methyl group of coordinated *re*1,2 propylene. (b) Interaction of methyl group in position 2 with methyl group of coordinated *si*1,2 propylene-filled bonds: out of the plane – to the reader, empty bonds behind the plane.

chain positions are favored than in the case of no methyl group at position 2. Interaction of methyl groups of Cp with the incoming monomer and of this with the growing polymer chain can affect the transition state for termination reactions due to steric reasons and alternative structure stabilization, with H located in the wrong position to be transferred to the Zr or to the monomer (see Fig. 7b).

In summary, we have certain active site structures in the soluble catalysts Cat1 and Cat2. Using SMAO and Cat1, some of the active site structures in the in situ immobilized system are similar to the soluble ones; new active sites are formed (with different structures), and the activity is highly decreased by the alkylaluminums. Using SMAO and Cat2, once again there is a group of sites similar to the soluble Cat2 and another one, characteristic of this in situ supported system that generates a more regioirregular/stereoirregular polypropylene. Here, the effect of the alkylaluminum is similar to that in the case of the Cat1 in terms of activity and molecular weight. This parallel effect, besides the steric hindrance, points to an additional electronic effect of the alkylaluminums.

The following sections will deal with the combined discussion of the experimental data and modeling. The following assignments are made:

1. The formation of inactive species of zirconocene upon contact with SMAO and the reactivation with the alkylaluminum.
2. The possibility of two different ligand distributions of the metallocene on SMAO (Sites 1 and 2 of Fig. 4), including the role of the alkylaluminum [42–48].
3. The role of the 2-methyl substitution in the metallocene in the *re*/*si* primary/secondary insertion in the Cat2 supported on SMAO for the two first insertions of propylene. The impact in the polymer microstructure.

We designed the molecular study to understand and to propose an explanation of the possible effect of Cp substitution in zirconocene at position 2 on the propylene coordination – from the steric point of view – at a local level on the supported systems Cat1 vs Cat2. In the case of the Cat2, we focused on the possible explanation of the second kind of polymer produced by the supported Cat2. To properly address the effect of the alkylaluminum, one must know the exact location and the electronic distribution around the zirconium center. We are planning to perform this kind of study in forthcoming papers.

The coordination of the propylene is proposed to be different in the soluble and in the SMAO-supported system. The active site is considered to be cationic, in which MAO plays the role of a counter ion. Besides, a second olefin – non-polymerizable – or another alkylaluminum stabilizes the active site. This "alternative" site could also be occupied by a solvent molecule, if this molecule is polar enough to displace the second propylene molecule or even another neutral AlR_3. The activity is roughly one order of magnitude higher for the soluble Cat2. This higher activity with higher steric hindrance can be related to the results of Terano et al. [34,35]. It seems counterintuitive that *higher steric* hindrance *increases* the activity.

Considering the present model, the methyl group can increase the propagation constant because of the stabilization of a particular way of insertion: the chain stationary insertion. This mode of insertion involves the continuous insertion of incoming monomers, without the reordering of the growing chain or the exchange of positions of the growing chain and the coordinated monomer. The insertion with the wrong enantioface is decreased and the propylene coordination and transition-state steps for insertion are similar in structure because of the presence of the methyl group in position 2 of the Cp in the soluble Cat2 system.

Table 2 shows the changes in steric energies for the different coordinations of the first propylene molecule, primary and secondary, *si* and *re*, for Cat1 and Cat2 in the supported model based on Fig. 5, with the SMAO similar to the structure shown in Fig. 1. It is clear from Table 2 that the first coordination of olefin in the Cat2 is energetically favored, as well as the transition states for different coordination.

In the case of Cat1, primary *re* and secondary *si* coordination are preferred, but primary *re* shows a lower difference in transition state–initial state (TS–IS) than secondary *si.* In the case of Cat2, secondary coordination is preferred and primary *si* and secondary *re* are the selected paths for insertion.

The supported Cat1 produces a more homogeneously stereoregular and regioregular polymer than supported Cat2, which produces polymers with two different melting points: one higher and another lower than that obtained with Cat1. The polymer obtained with the supported Cat2 is more heterogeneous in nature.

With the model of the supported active site in the case of Cat2, one can explain the second kind of polymer obtained with the Cat2/SMAO/alkylaluminum. In the case of Cat1, the soluble and supported catalysts produce a polymer with similar T_m. For Cat1, the supported active site is similar to the soluble one, but the activity (or the number of sites) is lower, probably due to steric reasons (the presence of SMAO).

With the supported Cat1 catalyst, the order of the polymerization activity is TEA < TIBA < IPRA for Al/Zr = 100 and it is inverted for Al/Zr = 500, where activities are lower. With supported Cat2 at Al/Zr = 100, TEA and IPRA afford the

Table 2
Change in steric energies upon propylene adsorption. Energies in Kcal/mol for step 5 in the generation of the active sites

Propylene coordination	Cat1		Cat2	
First insertion				
Primary *re*	−5.8		−6.3	
Primary *si*	−3.3		−6.1	
Secondary *re*	−5.5		−7.1	
Secondary *si*	−3.6		−7.4	
Second insertion		Distance Zr−C (olefin)		Distance Zr−C (olefin)
Primary *re*	−0.6	3.2	2.3	3.4
Primary *si*	2.2	3.9	4.2	3.5
Secondary *re*	1.9	4	−0.6	4.4
Secondary *si*	−0.9	4.3	−1.6	3.8
Second insertion. Difference steric energy transition state (TS)−initial state (IS)		Distance Zr−C (olefin)		Distance Zr−C(olefin)
Primary *re*	7.6	2.2	6.02	2.2
Primary *si*	6.22	2.3	2.4	2.2
Secondary *re*	8.2	2.3	4.8	2.3
Secondary *si*	9.5	2.3	7.8	2.3

same activity, whereas at Al/Zr = 500, activities are low in all cases. When 2-methyl substituted catalyst is analyzed, the active site of the soluble catalyst is totally different from the active site of the supported catalyst because of the presence of the SMAO as a ligand. With respect to the second insertions, the presence of the 2-Me renders easier the *re*2,1 or the *si*1,2 insertion in the case of this kind of catalyst vs the *re*1,2. After a *re*2,1 insertion, the idea is that the site remains inactive in the case of propylene polymerization. It is clear that *si*1,2 insertion would be favored if the methyl is placed in position 2 of Cp in the zirconocene, as is depicted in Fig. 7a and b and results from Table 2.

In the case of supported Cat1, the supported active sites have lower propagation constants and different termination to propagation constant ratios than in the case of the soluble one, but the microstructure obtained is very similar. We can consider several issues in this point. There are further possibilities for the propylene approach: two possibilities for the 1,2 insertion if the propylene molecule is coordinated in a plane located in the middle between the two indenyl, with the methyl up and down. In this case, we are considering that the key point to explain activity is that a new kind of site (with different ratios between the propagation constant and the termination constant) is formed. We can consider also the possibility of another distribution of the ligands and the formation of a soluble-like active site. In this case, the support and the chlorine would be *trans* to each other and the indenyl groups would not be located as far away from the support as they can be, but in close interaction with SMAO. The point is that this kind of site would be difficult to form in the case of supported Cat2 because of the steric hindrance induced by the methyl in position 2 (see Figs. 4 and 6).

Fig. 8a shows the similarity between the kinds of sites proposed in the soluble and supported system. These soluble-like species have been analyzed theoretically by Zurek and Ziegler [28]. The ligands marked with asterisk can exchange their positions. A ligand can be coordinated *trans* to the Al moiety from MAO on the support. In Fig. 8a, positions marked with an asterisk can be occupied by a dimer in the case of TEA, but only by 1 monomeric molecule of TIBA or IPRA due to steric reasons. There is no room to place 2 TIBA/IPRA molecules too close.

Since no MAO leaching is assumed to take place, this position is supposed to be occupied by an alkylaluminum (even TMA from MAO if SMAO can release TMA loosely bound, but this would be a small amount). The main difference between soluble and supported active site is that in the case of the supported one, the indenyl ligands changed their orientation, and SMAO is supposed to be more tight (less flexible) than in the case of soluble MAO for some active sites. Coordination of the alkylaluminum must have an important effect on the molar mass and on the propagation constant because of electronic/steric effects. The coordinating power (electronic effect) and the bulkiness (steric effect) must be considered in the analysis. Because IPRA and TIBA have lower coordinating power than TEA [35], especially at low concentrations, but have greater bulkiness, the different trends in the activity with the Al/Zr molar ratio for the different aluminum alkyls can be understood in the case of the in situ supported catalysts (Fig. 9).

Fig. 10 shows the steric hindrance induced by the alkylaluminum coordination and how it affects the polymerization termination reaction. The β-methyl transfer reaction is difficult. In the case of TEA, the effect is not as strong as in the case of IPRA or TIBA. When the supported Cat2 is analyzed, the presence of methyl group in position 2 partially hinders the formation of the ''soluble-like'' active site. Considering the results shown in Table 1, this kind of site is present when Cat2 is used in the presence of no sterically demanding structures.

The presence of the second kind of active site, with the structure proposed above in Fig. 3, can explain the second melting point and the broadening of the polydispersity in the case of supported Cat2. This kind of active site cannot be ruled out in the case of supported Cat1. The key point of the similarities of the produced polymer can be explained using the concept of Chien about the importance of the ratio between

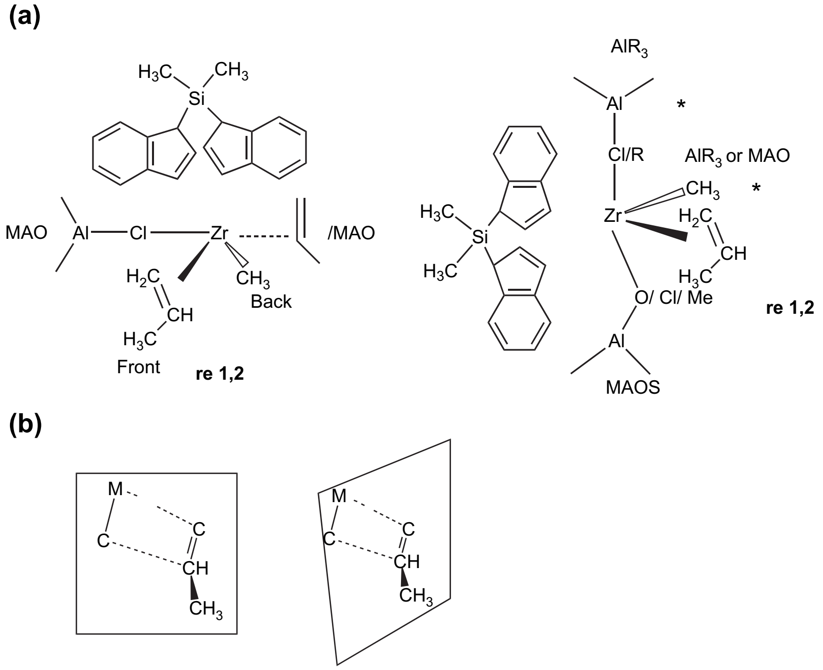


Fig. 8. (a) Proposed supported "soluble-like" active site in the case of the Cat1 catalyst. (b) Comparison of the coordination of propylene in the soluble-like and supported-like active sites.

the propagation and the termination constant in the polydispersity [43]. Several different sites can produce a polymer with the polydispersity near 2, considering that the propagation to termination constants ratio is similar for these sites in different structures. The idea of different active sites in a supported zirconocene has been recently reported for Cp_2ZrCl_2 grafted on montmorillonite [44].

According to Brintzinger et al. [47] irregularities introduced in the polypropylene chain due to 1,3 and/or 2,1 insertions decrease its melting point. The molar mass of the polymers decreased in the order TIBA > IPRA > TEA for high Al/Zr molar ratio for both catalysts, being more pronounced in the case of the substituted metallocene. According to Michaels and Munõz-Escalona [48] this behavior was expected: bulky ligands of the alkylaluminum reduce the termination rate by chain transfer, increasing the molar mass. We think that, rather than hindering the methyl transfer reaction to the alkylaluminum, the alkylaluminum is hindering the termination reaction (H-transfer to monomer).

To confirm the idea that stereoirregularities are higher for the supported than for the soluble catalysts, two samples of PP with similar molecular weights, obtained with Cat2, soluble and supported, were analyzed. Table 3 shows the results of ^{13}C NMR for polypropylenes obtained with Cat2, soluble and supported, with IPRA as the alkylaluminum in Al(IPRA)/Zr = 100. The heterogeneous catalyst showed a lower concentration of isotactic diads (mm) and higher concentration of syndiotactic (mr) and atactic (rr) ones. This result

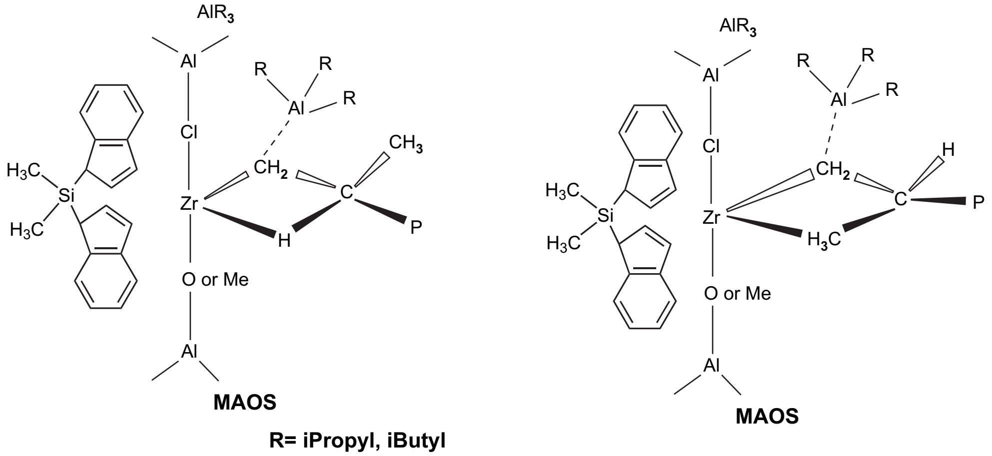


Fig. 9. Transition states for termination reactions for soluble-like active site-H would be available for the incoming monomer.

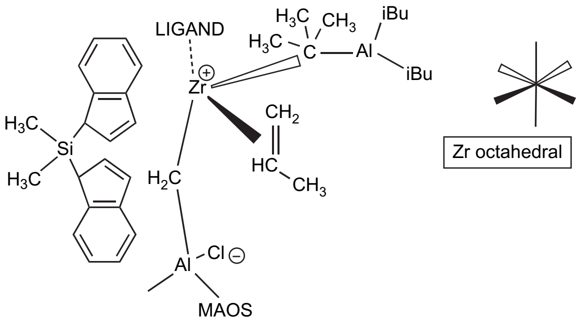


Fig. 10. Steric interactions in supported species in presence of alkylaluminum. Zr bonds to Cp centroids not included for the sake of clarity. Filled bonds: out of the plane – to the reader, empty bonds behind the plane – simple bonds on the plane.

Table 3
^{13}C NMR data for homogeneous (PP 306) vs heterogeneous (PP 311) catalyst with IPRA as alkylaluminum and Al(IPRA)/Zr = 100

%m Pentads/% diads	PP 306	PP 311
mmmm	87.3	80.1
mm	94.5	89.9
mmmr	5.1	9.8 (+rmmr)
rmmr	2.1	–
mmrr + mmrm	3.5	4.2
mr	4.00	7.5
rmrr	0.5	3.3 (+rmrm)
rmrm	0.0	–
rrrr	0.1	0.4
mrrm	1.2	1.8
rrrm	0.2	0.4
rr	1.5	2.6

strongly supports our proposal. All the parameters that indicate stereoirregularities are higher in the supported catalyst vs the homogeneous one. For Cat2, this finding is the common trend (see Table 1).

5. Conclusion

Experimental data of in situ supported catalysts and polymer produced by soluble and supported Cat1 and Cat2 were analyzed with the most recent theories on active site formation. The proposition of two different sites in the ''in situ'' supported Cat2 and Cat1 allows us to explain the trends in activity and molar mass and structure found for these catalysts. The two kinds of sites are one group of ''soluble-like'' sites and another group of ''truly MAO-supported'' sites, similar in structure to those supported on bare silica, but not in activity. TEA, TIBA and IPRA have different effects on the activity, the molar mass and the polydispersity depending on the zirconocene structure. These findings support the idea of the importance of the MAO/alkylaluminum as a modifier of the active site and not only a simple counter ion. Molecular modeling results and ^{13}C NMR of selected samples of homogeneous and heterogeneous catalyst are in agreement with the proposed ideas.

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