



Polypropylene obtained with in situ supported metallocene catalysts

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Abstract

Propylene homopolymerization was carried out with $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ immobilized on commercial MAO-modified silica by the in situ supporting technique. Adsorption isotherm determination for this metallocene on silica indicated that the saturation level is reached at 2.0 wt.% Zr/SMAO. Catalyst systems were shown to be active in the absence of external MAO, being activated by common alkylaluminum cocatalysts, namely triethylaluminum (TEA), isoprenylaluminum (IPRA) and triisobutylaluminum (TIBA). The effect of the nature and concentration of cocatalyst on catalyst activity and on polypropylene (PP) properties was evaluated. Best catalyst activity was observed in low concentration of IPRA (1.4 kg PP/g cat h). The resulting polymers were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and scanning electronic microscopy (SEM).

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1. Introduction

The development of metallocene catalysts represented a new step in the polymerization field. Polymers produced by metallocene catalysts have a different architecture compared to conventional polymers ob-

tained by Ziegler–Natta catalysts. Among the advantages of these systems are the unique properties of the new resins, such as narrow molecular weight and uniform comonomer distributions. Moreover, the adaptability of metallocene catalysts to existing plants, the potential for product/property modifications through rational catalyst manipulations, and an increasing pace of discovery through new research methodologies are also very attractive features of these catalysts (see, for example [1]).

Polyethylene, polypropylene (PP) and copolymers with higher α -olefins are already produced industrially

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by metallocene catalysts but still on small scale, since there are still some drawbacks that have to be overcome, such as difficulty in controlling polymer morphology and the large amount of MAO necessary to achieve high activity and keep catalyst stability. The heterogeneization of metallocenes has been researched extensively and proposed as an alternative to overcome such problems. There are many routes described in the literature employing different supports, immobilization procedures (grafting, wet impregnation), surface chemical modification (alkylaluminum, organosilicon), just to mention a few [2].

Although heterogeneous systems present some advantages over the homogeneous ones, the activity of supported metallocenes is generally reduced in comparison to those of homogeneous systems. Many reasons have been attributed to this decreased activity, such as the generation of only 1.0% of the total grafted content as active species [3] and steric effects of the silica surface, which plays the role of a huge ligand. Moreover, zirconocene extraction from the silica surface by MAO has been pointed out as a disadvantage that must be overcome if supported catalysts are to be used successfully. Some alternatives have been proposed to overcome these problems, such as the use of surface spacers which keep the zirconocene centers farther from the surface [4], the use of horizontal spacers which reduce bimolecular deactivation reactions [5], and the direct synthesis of metallocenes on inorganic–organic hybrid silica [6].

All the proposed supported procedures are time demanding, involving reaction and washing steps and final catalyst characterization. Soares et al. proposed an alternative methodology (in situ supporting) which uses a commercial immobilized cocatalyst [7]. This approach consists in the direct addition of the catalyst solution to the MAO-supported silica inside the reactor, just before pressurizing with monomer. No additional MAO is required since common alkylaluminum cocatalysts can activate in situ supported catalysts. Therefore, this procedure avoids time consuming steps or addition of external MAO. Supported catalysts prepared by this in situ immobilization technique have been evaluated for ethylene homo- and copolymerization [8–11]. In the present work, we studied propylene homopolymerization employing *rac*-dimethylsilylenebis(indenyl)zirconium dichloride ($\text{Me}_2\text{Si}(\text{Ind})_2\text{-ZrCl}_2$) as catalyst and commercial MAO-modified

silica (SMAO) support. The effect of common alkylaluminum cocatalysts was evaluated on catalyst activity and polymer properties. Adsorption isotherm measurements were performed to determine the surface saturation content for this metallocene. Resulting polymers were characterized by differential thermal calorimetry (DSC), gel permeation chromatography (GPC), ^{13}C nuclear magnetic resonance (NMR) spectroscopy and scanning electronic microscopy (SEM).

2. Experimental

2.1. Materials

All the experiments were performed under inert atmosphere using Schlenk techniques. The catalyst *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (Witco), MAO-supported silica (SMAO, 23 wt.% Al, Witco), 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 and by distillation. Hexane was degassed by bubbling nitrogen before each reaction.

2.2. Adsorption isotherm determination

Several initial catalyst solutions (0.5–5.0 wt.% Zr/SMAO) were contacted with SMAO at 60 °C for 1 h. The resulting slurry was washed with 15 × 2 ml of toluene, vacuum dried, and the final metal content in the resulting solid was determined by Rutherford backscattering spectrometry (RBS), according to the standard procedure described elsewhere [12]. For comparative reasons, polypropylene produced by these catalysts was analyzed by scanning electronic microscopy micrography and compared to those produced by homogeneous and in situ supported catalysts.

2.3. Polymerization

Polymerizations were performed in a 1.5 l stainless-steel reactor equipped with mechanical stirrer, constant temperature circulator and inlets for argon and for propylene. The reactor was filled with SMAO

(Al/Zr = 500 (mol/mol)), 0.75 l of hexane, 10 ml of catalyst solution (10^{-5} mol catalyst in toluene) and alkylaluminum. When the mixture reached 60 °C, the reactor was pressurized with propylene up to 6.0 bar (partial pressure) for 60 min. The polymer was precipitated by acidified (HCl) ethanol. Homogeneous polymerizations were performed under the same conditions using MAO (Al/Zr = 500 and 2000) as cocatalyst, instead of the alkylaluminum.

2.4. Polymer characterization

Crystallinity (χ), melting (T_m) and crystallization (T_c) temperatures were determined using a TA Instruments 2920 differential scanning calorimeter, according to ASTM D 3417/97 and ASTM D 3418/97. Two scans were performed, but only the results of the second scan were reported. The heating rate was 10 °C/min in the temperature range from 30 to 220 °C. Molecular weight distributions were determined by high temperature gel permeation chromatography using a 150 C Waters instrument equipped with four columns GMHXL-HT (TosoHaas) at 138 °C. 1,2,4-Trichlorobenzene was used as mobile phase. The columns were calibrated with 18 polystyrene and 3 polyethylene standards.

Polymer microstructure was determined by ^{13}C NMR. The spectra were obtained at 135 °C in a Varian Inova 300 operating at 75 MHz. Sample solution of the polymer were prepared in *o*-dichlorobenzene (ODCB) and benzene- d_6 (20% (v/v)) in 5 mm sample tubes. Spectra were taken with a 74° flip angle, in an acquisition time of 1.5 s and a delay of 4.0 s.

Scanning electronic microscopy analyses were performed using a DSM-940 Zeiss instrument operating at 3–4 kV. Samples were prepared as films sputter-coated with gold (20 nm thickness). Images magnification was 2000 \times .

3. Results and discussion

Many catalyst supporting techniques are reported in the literature, differing on the immobilization procedure, as well as the resulting properties and goals of the final catalyst [13]. In the specific case of supported metallocene catalysts, two routes are important, namely grafting and impregnation, since in the present

case the maintenance of the coordination sphere is mandatory for the catalyst application. Grafting reaction implies in the chemical reaction between the catalyst and the support, followed by washing steps in order to remove non-reacted, physically adsorbed catalysts. Impregnation is a faster method, in which support and catalyst solution are put into contact. The solvent is removed, but the resulting catalyst is not washed: the initial amount of catalyst might remain totally in the solid, whether chemically reacted or just physically adsorbed. The maximum loading of a surface with a certain catalyst can be obtained by determining its adsorption isotherm, in which different initial catalyst concentrations are put into contact with the support, followed by washing, grafting, and drying steps. Afterwards the final metal content is measured.

We have previously determined Cp_2ZrCl_2 , TMA and MAO adsorption isotherms on different commercial silicas [14]. Since in the present approach the catalyst is directly contacted with the support inside the reactor, it is expected that the amount of catalyst impregnated is less than the saturation level of the catalyst on the support. Therefore, we initially determined the adsorption isotherm of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ on the SMAO support.

Fig. 1 shows the adsorption isotherm at 60 °C, the same temperature used for the polymerizations. According to Fig. 1, the saturation level is reached at ca. 2.0 wt.% Zr/SMAO. It is worth mentioning that for initial concentrations lower than the saturation level, almost all the catalyst present in the solution is adsorbed onto the support. Such behavior is typical of strong interaction between the catalyst and the support [15].

The in situ procedure was tested for a ratio of Al/Zr = 500, which is below the saturation level of Al/Zr = 40. It is worth noting that Al/Zr = 500 represents a lower Zr content in comparison to that of Al/Zr = 40, keeping the Al content constant. The effect of the nature and amount of the cocatalyst on catalyst activity is shown in Table 1. Three cocatalysts were evaluated, namely TEA, IPRA, and TIBA, in the range between 0.7 and 20.0 mmol, corresponding to Al/Zr comprised between 70 and 2000 (mol/mol) of external aluminum.

Among the three cocatalysts investigated, IPRA led to the highest activity system. The activity was roughly two or three times higher than those observed for the two other systems. In the case of IPRA, catalyst

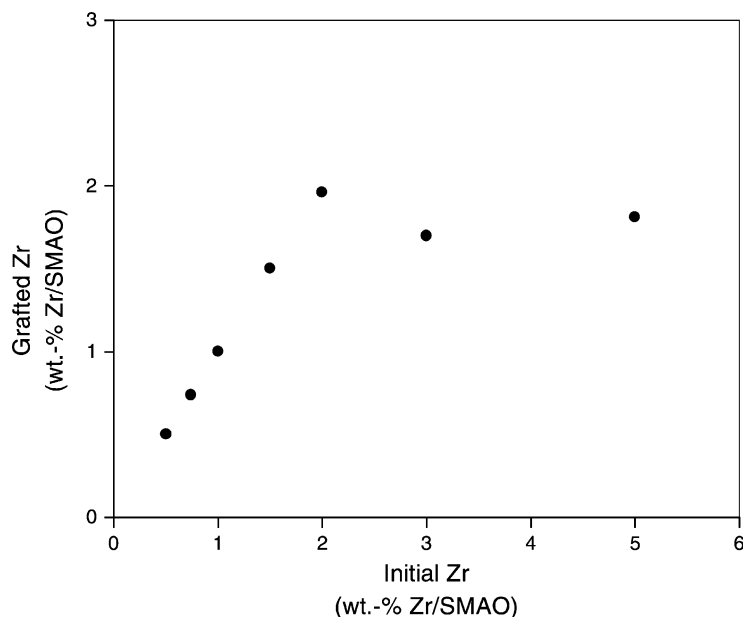


Fig. 1. Adsorption isotherm of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ on SMAO (Witco). Grafting reaction performed in toluene at 60°C .

activity decreased as the cocatalyst amount increased. For TEA and TIBA, the catalytic activity was almost constant for the different amounts of cocatalyst, decreasing for values higher than 5.0 mmol. A plausible polymerization mechanism explaining the role of alkylaluminum as scavenger, alkylating agent and cocatalyst activator with in situ supported metallocenes has been reported [10]. Lower catalyst activity in the ethylene polymerization with in situ supported $\text{EtInd}_2\text{ZrCl}_2$ was also reported in the case of TEA

and TIBA cocatalysts [11]. Polymerization tests with ex situ catalysts, using TIBA as cocatalysts showed similar results.

For comparative reasons, homogeneous reactions using MAO as cocatalyst ($\text{Al}/\text{Zr} = 500$) were also performed producing 4.6 kg PP/g cat h, i.e. almost three times higher than the highest activity observed in the case of IPRA and in situ supported catalyst. Higher Al/Zr ratio ($\text{Al}/\text{Zr} = 2000$) led to more active systems, producing 13.0 kg PP/g cat h.

This behavior, has been reported several times in the literature. The decrease in catalyst activity has been attributed to generation of inactive species on the support surface and/or to diffusion limitations during polymerization [3]. Considering both homogeneous systems, the increase in activity from $\text{Al}/\text{Zr} = 500$ to 2000 was already observed in the literature for similar cocatalyst ranges and might be attributed to the various roles of MAO during polymerization. The role of MAO as cocatalyst is not still clearly elucidated, and many roles have been attributed to this compound, such as alkylation of the catalyst, stabilization of the cationic metallocene alkyl by acting as a counter-ion, and the prevention of bimolecular reduction of the catalyst. Moreover, MAO can scavenge impurities such

Table 1

Catalyst activities of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{SMAO}$ system in the presence of different alkylcocatalysts

Alkylaluminum, Al/Zr^a (mol/mol)	Activity (kg PP/g cat h)		
	TEA	IPRA	TIBA
70	0.3	1.4	0.5
130	0.4	0.8	0.4
250	0.4	0.1	0.6
500	0.3	0.2	0.2
1000	0.1	0.1	0.2
2000	0.2	np	np

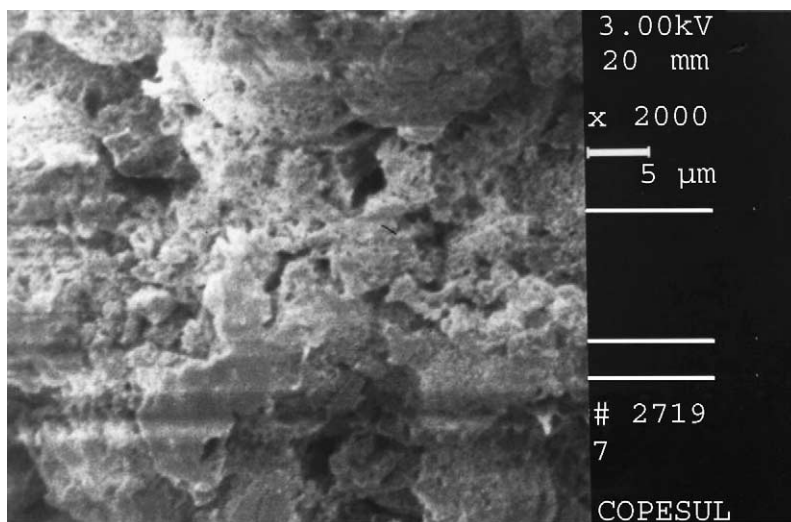
np: not performed; homogeneous reactions using MAO as cocatalyst ($\text{Al}/\text{Zr} = 500$) produced 4.6 kg PP/g cat h.

^a External aluminum.

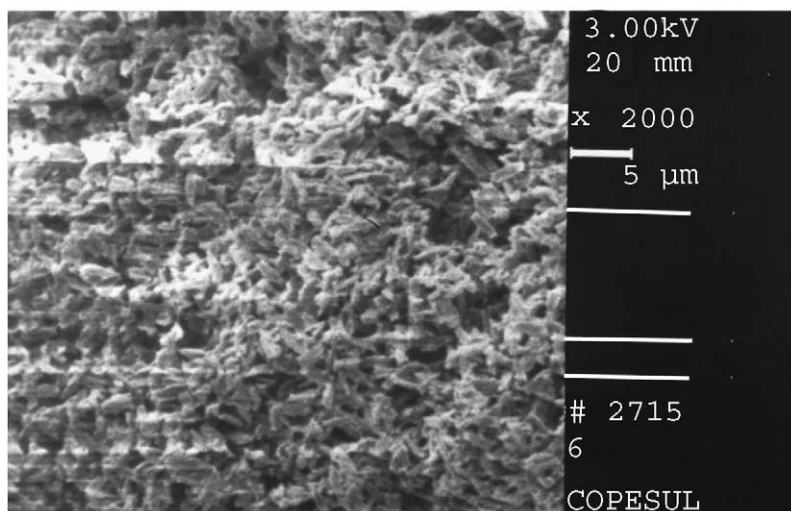
as water and oxygen from the reaction milieu (see, for example [16]).

The resulting polymers were characterized by DSC, GPC and ^{13}C NMR (Table 2). DSC results show that the polymers obtained with the in situ supported catalyst system have a lower melting temperature (T_m), crystallization temperature (T_c) and crystallinity, than those made with the homogeneous systems. On the

other hand, the polymers produced via in situ supported catalyst exhibited higher MW than those obtained with the homogeneous system using $\text{Al/Zr} = 500$. This behavior has already been observed [17] and attributed to blocking of one of the sides of polymerization active sites by the support, hindering the deactivation step. In other words, β -elimination transfer between two metallocene centers is hindered,

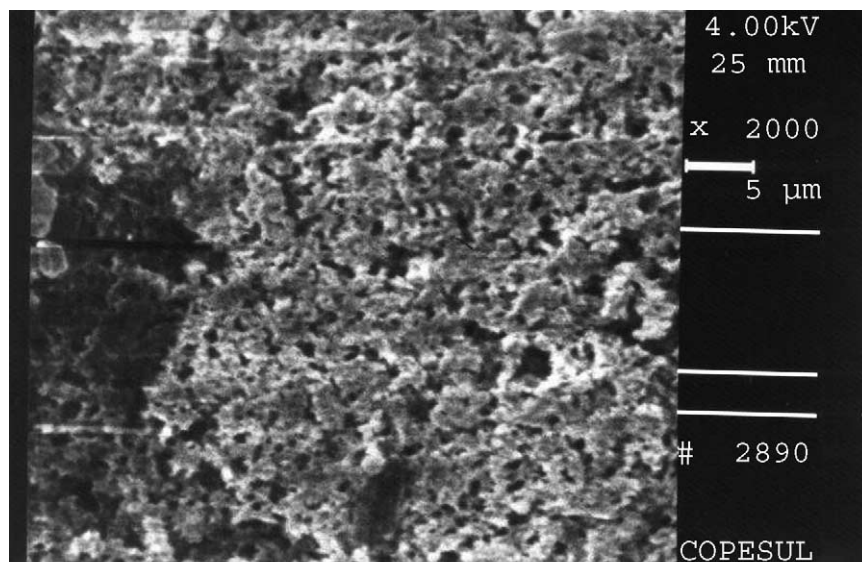


(a)



(b)

Fig. 2. Micrographs of SEM (2000 \times) of the polymers obtained with $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$: (a) homogeneous, (b) in situ supported catalysts system, and (c) ex situ supported catalysts system.



(c)

Fig. 2. (Continued).

resulting in a larger growth of the polymer chain, and therefore in higher molecular weight [18]. Since polymers with high average molecular weights show better mechanical properties than those with low average molecular weights, this is an attractive feature of supported metallocene catalysts in general, and in situ supported catalysts in particular.

Molecular weight depends on alkylaluminum type, decreasing in the following order: TIBA > IPRA > TEA. Similar results were observed in the case of polyethylenes produced with in situ supported $\text{Et}[\text{Ind}_2\text{ZrCl}_2]$ [11].

The polymers produced with in situ supported catalyst had a polydispersity index only slightly

higher than the polymers made with homogeneous systems, suggesting that the single-site character of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ is kept in the in situ immobilization.

The tacticity of polypropylene was calculated by ^{13}C NMR. The percentage of dyads (m) is also presented in Table 2. All the polymers were highly isotactic ($m = 94.0\%$) and the stereoregularity seems not to be affected by the nature of the cocatalyst or by the supporting procedure. The control of stereoregularity of polypropylene is very important because it is directly related with properties such as mechanical strength, hardness, impact resistance and transparency of the polymer.

Table 2

Polymer properties of PP obtained with homogeneous and supported $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{SMAO}$ system

System	T_m (°C)	T_c (°C)	χ (%)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n	m (%)
TEA (in situ) ^a	139	106	29	18600	40000	73000	2.2	94.0
IPRA (in situ) ^a	137	108	42	20100	44000	84000	2.2	92.7
TIBA (in situ) ^a	140	105	36	29800	67000	117000	2.2	94.0
IPRA (ex situ) ^a	135	102	39	19800	41000	73000	2.1	–
Homogeneous (Al/Zr = 500)	142	110	53	16400	34000	55000	2.1	–
Homogeneous (Al/Zr = 2000)	142	110	52	21300	44000	70000	2.1	94.0

^a Al/Zr = 130 (external aluminum).

The morphology of the polymers obtained by both homogeneous and supported catalysts was examined by SEM. According to Fig. 2, a micrograph of the polymer made with the homogeneous catalyst shows a conglomerate of crystalline polypropylene without any morphological control (Fig. 2a). On the other hand, the polymer obtained using SMAO-in situ immobilization (Fig. 2b), presented the same homogeneity in porosity showed by the polymer produced with the ex situ supported catalyst, i.e. prepared by conventional grafting procedure (Fig. 2c), suggesting that the polymerization took place effectively on the silica support. Besides, the polymers obtained with the in situ and the ex situ supporting procedure presented similar properties, as shown in Table 2.

4. Conclusions

In situ supported $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ prepared by direct contact of metallocene with SMAO in the reactor generates a catalyst system that is active for propylene polymerization in the presence of simple alkylaluminum cocatalysts such as TEA, TIBA, and IPRA. Considering that the saturation level of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ on SMAO is reached with 2.0 wt.% Zr/SMAO, the employed Al/Zr ratio of 500 (mol/mol) enhances the likelihood that the metallocene catalyst might have grafted on the support surface or at least will not be significantly extracted during polymerization.

Polymers obtained with the in situ supported catalyst had lower T_m , T_c , and crystallinity than those made with the homogeneous catalyst. On the other hand, polymers produced by the in situ supported systems had higher molecular weights than those synthesized with the homogeneous catalyst at the same Al/Zr ratio. Tacticity does not vary with the catalytic system, showing that the stereoselectivity of the catalyst was not affected by the support. Besides, SEM micrographs showed that polymers obtained with the in situ and conventionally supported systems presented a defined morphology, conversely to polymers obtained with the homogeneous system, confirming that there is no significant extraction of the catalyst from the silica support during polymerization of propylene.

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