Study of some parameters on the zirconocene immobilization over silica

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Abstract

This work presents a 2^{3-1} factorial planning designed to evaluate the effect of some parameters of the metallocene immobilization route in the ethylene polymerization. The highest ethylene polymerization activity was observed for the catalyst synthesized using TMA as modifier agent, in the inverse addition order, and impregnation temperature of $60\,°C$. These results indicated that the immobilization route played an important role on the catalysts performance. UV-Vis DRS results suggested the formation of MAO-like species on the silica surface. These species may be formed from the reaction of TMA either with water adsorbed on the support or OH groups of the silica surface. DSC analyses indicated that the crystallinity of these polymers varied as a function of the catalytic activity, the more active catalysts producing polymers with higher crystallinity. The obtained polymers presented melting point around $133\,°C$, typical of commercial polyethylene.
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1. Introduction

The metallocenes have become an important class of catalysts for olefin polymerization, due to the possibility of modeling the molecular structure of the polymers [1]. In comparison with the conventional Ziegler–Natta catalysts, the metallocene-based systems offer a great versatility and flexibility in the synthesis and control of the polyolefin structure [2]. Moreover, due to the fact of being single site, these systems present the advantage of producing polymers with narrow distribution of molecular weight and uniform incorporation of co-monomer [3–8].

Despite these advantages, metallocenes in homogeneous phase have some limitations for industrial use, specially in gas phase processes [2,4,6]. The most common problems are the difficulty in the polymer morphology control, the formation of fouling in the reactor and the great amount of co-catalyst necessary to obtain a high catalytic activity [2,9]. The immobilization of metallocenes on inorganic supports has been proposed to solve these problems. The goal is to provide the immobilization of metallocenes without modifying their properties such as high catalytic activity, stereochemical control, polymer with statistic distribution of co-monomer, while improving the polymers morphology [2,10].

Many studies developed to supported metallocenes [9–14] indicated that the nature of the support as well as the technique used to support the metallocene, plays an important role in the catalytic activity and in the final properties of the polymers, such as morphology and molecular weight distribution. Furthermore, morphology studies of polymers obtained with metallocenes anchored in different supports [1,15–17] indicated a direct relation between the polymer and support morphology.

In this context, the aim of this work is to verify the effect of different anchoring routes of metallocene over silica, using an experimental planning, on the catalytic activity in the ethylene polymerization and the final characteristics of polymer.

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2. Experimental

2.1. Reagents

Toluene and *n*-heptane (Merck, of 99% purity), previously dried, were used as solvents, the catalyst support was silica Grace 952 ($256\,m^2$/g BET surface area), calcined by 2 h at $200\,°C$ under flow of nitrogen UP (Air Products). The modifier agents were trimethylaluminum, TMA (4.7% (w/w) of Al in toluene) and methylaluminoxane, MAO (7.2% (w/w) of Al in *n*-heptane), both from Akzo Nobel, and handled under nitrogen atmosphere. The metallocene [$(Cp)_2ZrCl_2$] of 99% purity was supplied by Strem Chemicals and ethylene polymer grade (humidity below 3 ppm) was manufactured by Braskem Petrochemical. In all stages of the catalyst synthesis, it was used Schlenk technique to avoid the deactivation of the reagents by contact with the air.

2.2. Catalyst preparation

The catalysts were synthesized according to different experimental procedures in order to study the effect of the metallocene immobilization route on catalyst activity and in the characteristics of the polymers obtained. A 2^{3-1} factorial experimental planning was carried out and the following parameters were evaluated: type of modifier agent (TMA or MAO), addition order of the modifier agent (direct modifier agent over the silica or inverse—silica over the modifier agent) and temperature of metallocene impregnation over modified silica (30 or $60\,°C$). The response used was catalytic activity in ethylene polymerization. Table 1 describes the levels attributed to those variables.

The catalysts were synthesized according to the following method: a suspension of silica in toluene was maintained in contact with the modifier agent (MAO or TMA) during 1 h at $30\,°C$, under magnetic stirring. The aluminum content was 2.74 mmol. After that, the treated silica was filtered and washed with toluene for removing the modifier agent excess. A solution of [$(Cp)_2ZrCl_2$] catalyst in toluene was then added to the treated silica. That suspension was stirred and heated for 2 h at 30 or $60\,°C$, according to the route used. At the end, the heterogeneous catalyst obtained was filtered, washed with toluene for removal of metallocene excess, dried and tested in ethylene polymerization. Table 2 presents the synthesis conditions for each one of the catalysts prepared in this work.

Table 1
Experimental domain of the variables

Variable	Level	
	(−)	(+)
X_1—Order of addition	Direct	Inverse
X_2—Type of modifier agent	TMA	MAO
X_3—Temperature of metallocene impregnation (°C)	30	60

Table 2
Synthesis conditions of the catalysts

Experiment	X_1	X_2	X_3 (°C)	Catalyst
1	Inverse	MAO	30	SZ–09
2	Direct	MAO	60	SZ–10
3	Inverse	TMA	60	SZ–11
4	Direct	TMA	30	SZ–12

2.3. Characterization

The zirconium contents in the catalysts were determined by the technique of ICP-OES, from samples dissolved in fluoridric acid.

For a systematic identification of the species that were formed during the several stages of the metallocenes immobilization, the reference samples TMA/SiO_2 and MAO/SiO_2 were prepared, both in direct (AD) and inverse (AI) order of the modifier agent addition; these samples were analyzed by UV-Vis DRS technique. The powder sample spectra, in the region from 2500 to 200 nm, were obtained with a scanning rate of 500 nm/min, using a spectrophotometer Cary-5E Varian coupled with a module for diffuse reflectance spectroscopy (DRS).

The melting point and the crystallinity of the produced resins were obtained by DSC technique, using a thermal analyzer Shimadzu TA-50, from $40\,°C$ to $200\,°C$, with heating rate of $10\,°C$/min, under nitrogen atmosphere.

Micrographs of the original support and the polymeric particles were obtained by scanning electronic microscopy (SEM), using a Zeiss model DSM-240A.

2.4. Catalytic tests

All catalysts were tested in ethylene polymerization reaction, in a laboratory scale reactor. The ethylene polymerization procedure was as follows: toluene was added to a glass reactor of 300 ml, equipped with a thermostatic bath and a mechanical stirrer, under inert nitrogen atmosphere, followed by MAO and the catalyst containing 0.01 mmol of zirconium. The reactor was maintained under a constant pressure of ethylene, with stirring and controlled temperature of $50\,°C$, during 1 h. The polymer obtained was filtered, dried and then stored for subsequent characterization.

3. Results and discussion

3.1. Effect of the preparation route on the catalytic activity

Table 3 presents the zirconium loading and activity in ethylene polymerization for both the commercial homogeneous [$(Cp)_2ZrCl_2$] and the prepared silica supported catalysts, as well as some physical properties of the obtained polymers.

The catalytic activity observed for the homogeneous [$(Cp)_2ZrCl_2$] was always higher than those presented by

Table 3
Catalytic activity and properties of polyethylene

Catalyst	$(Cp)_2ZrCl_2$	SZ–09	SZ–10	SZ–11	SZ–12
Zr (w/w%)	31	0.9	1.0	0.9	1.0
Activity (Kg_{PE} mol $Zr^{-1} h^{-1} atm^{-1}$)	895	164	97	657	229
Tm polymer (°C)	132	133	133	133	134
Polymer crystallinity (%)	55	50	30	61	54

Polymerization conditions: Al/Zr; relation: 500 (1000 for homogeneous); reaction temperature: 50 °C; solvent: toluene; and ethylene pressure: 1 atm.

Table 4
Effect of the variable in the activity of the catalyst

Variable	Coefficient
X_1	247.5
X_2	−312.5
X_3	180.5

the supported catalysts. Among the supported catalysts, the sample SZ-11, synthesized with TMA in inverse addition order and using a metallocene impregnation temperature of 60 °C, presented the highest activity for the ethylene polymerization. Furthermore, all catalysts synthesized using TMA as modifier agent presented higher catalytic activity than those synthesized using MAO, under the same polymerization conditions. These results indicated that the immobilization route played an important role in the activity of the obtained catalysts. Such results are in agreement with the literature [9–14].

The effects played by each studied variable on the catalyst activity are presented in Table 4. They were calculated by the average of the difference between superior and inferior levels. Such procedures evaluated the influence of each variable on the catalytic activity. The change of the addition order of the modifier agent from direct to inverse increased the activity by a factor of 2.5. Additionally, the use of TMA instead of MAO as the modifier agent increased the activity by 3.4. Regarding the impregnation temperature, the activity increased by 1.9 when the temperature changed from 30 to 60 °C. These results indicated that the nature of the modifier agent was the immobilization variable that most affected the catalytic activity.

The catalytic activity can be related to both the nature and the concentration of the species formed on the surface during immobilization. Fig. 1 presents the UV-Vis DRS spectra obtained with the four reference samples, as follows: silica modified with MAO and TMA, each modifier agent added in direct (AD) and inverse (AI) order. All spectra are shown as difference spectra. The toluene/silica spectrum was subtracted from each sample spectrum to prevent peaks associated with the toluene used in the sample preparation. All spectra show an absorption peak, around 290 nm, with variable intensity. This peak was also observed by Haag et al. [18] and attributed to MAO on the silica surface. Furthermore, in spite of the fact that the technique employed was not quantitative, the most active supported catalyst (sample SZ-11, Table 3) exhibited the most intense absorptive peak at 290 nm (Fig. 1).

Fig. 2 presents the deconvolution of the spectrum obtained for the silica modified with TMA in inverse addition order. The band at 290 nm was attributed to MAO species formed on the silica surface; the other bands at 220 and 250 nm were attributed to the silica support and the one at 330 nm to residual toluene. The formation of species with structure similar to MAO might occur on the silica surface, as illustrated in Scheme 1. TMA might react either with adsorbed water on the support or with hydroxyl groups of the silica surface, both reactions forming MAO species [19–21].
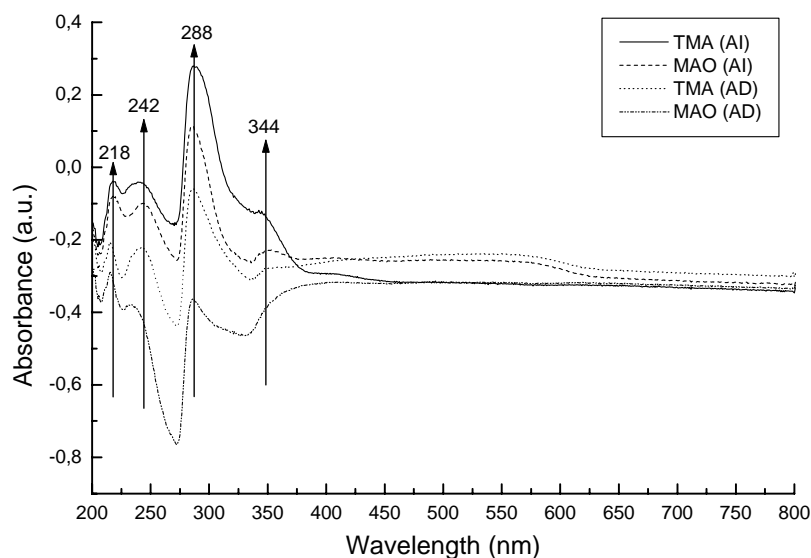

Fig. 1. Overlapping of UV-Vis DRS spectra of the silica modified with TMA or MAO, direct (AD) and inverse (AI) addition.
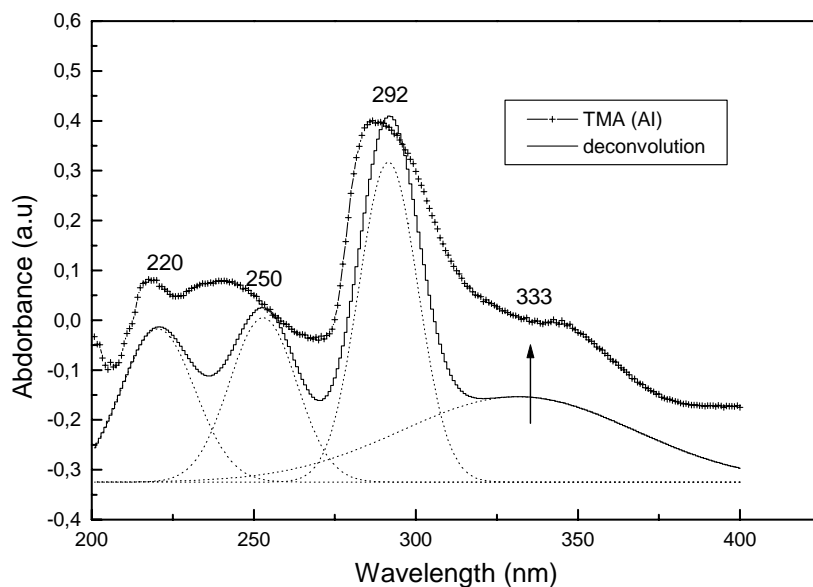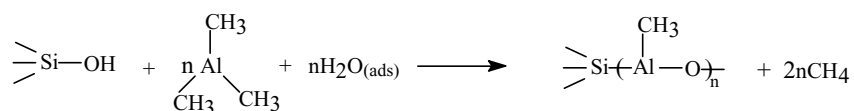
Fig. 2. Deconvolution of the TMA modified silica in inverse addition order spectrum.

Scheme 1. Reaction of TMA with silica based on [23].

The influence of the addition order on the catalytic activity might be due to local concentration effects. In the direct order, the modifier agent is added to the silica suspension, and the toluene in contact with or adsorbed on the silica surface prevents its diffusion to the surface. In the inverse addition order, the modifier agent itself was dissolved in toluene, causing higher local concentration, and therefore enhancing its interaction with the surface hydroxyl groups. These results are in agreement with previous ones reported in [2,22].

3.2. Effect of the preparation route on the characteristics of the polymers

Fig. 3 presents the micrographs of the polyethylene obtained with the homogeneous phase catalyst and the SZ-09 supported catalyst. The comparison of the two micrographs shows that the polyethylene obtained with the homogeneous phase catalyst had a more porous texture, while that obtained with the heterogeneous catalyst presented a compact texture. Hence, the metallocene
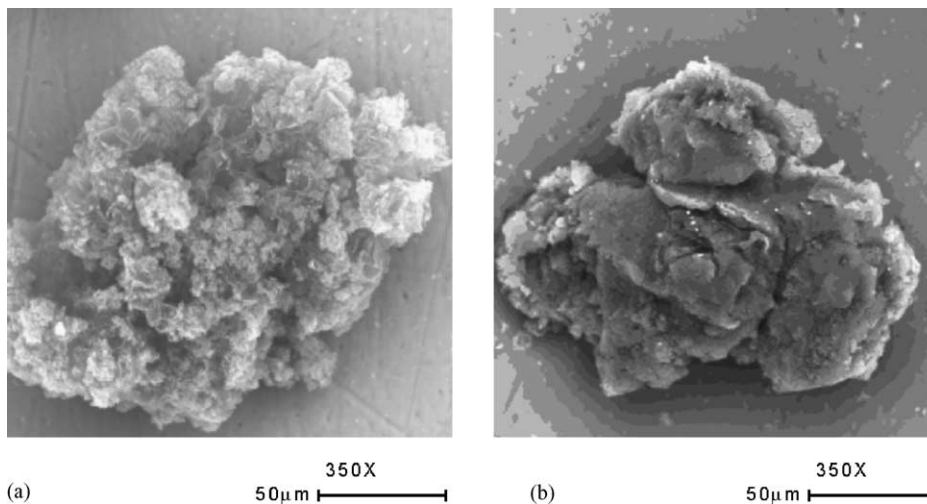

Fig. 3. (a) Micrograph of the polymer obtained with the catalyst $(Cp)_2ZrCl_2$. (b) Micrograph of the polymer obtained with the supported catalyst SZ-09.
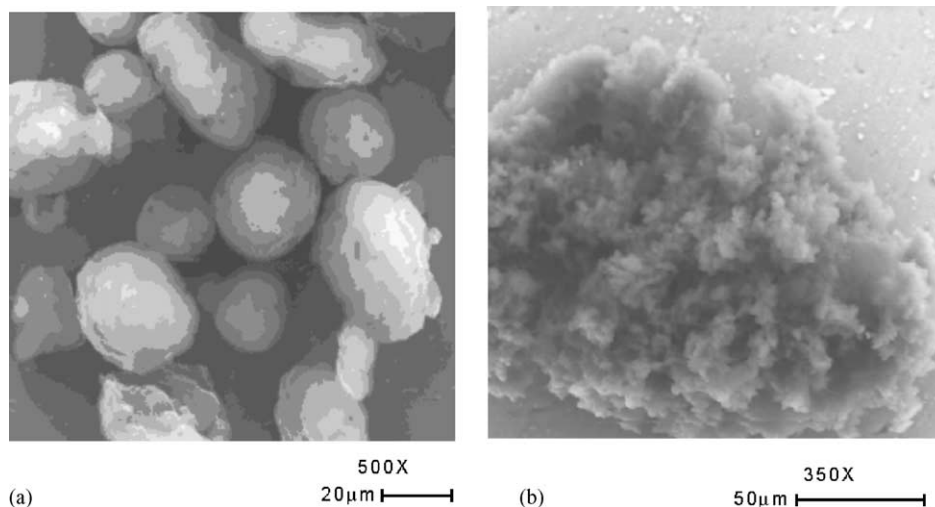
Fig. 4. (a) Micrograph of the silica. (b) Micrograph of polymer obtained with the supported catalyst SZ-11.

immobilization affected the texture of the polyethylene obtained.

Fig. 4 presents the micrographs of the silica support and the polyethylene obtained with the supported catalyst SZ-11. The silica micrograph shows predominantly round and oval particles with little size variation. Likewise, the polyethylene resin grew as particles of regular round and oval shape, similar to the silica support, in agreement with published results [1,15].

All synthesized polymers presented melting points around 132–134 °C, typical of commercial polyethylene (Table 3). Regarding to the polymer crystallinity, measured by DSC technique, the average value was 53%, excluding the least crystalline polymer. Additionally, the DSC analyses indicated that the crystallinity presented by those polymers varied as function of the catalytic activity for the supported systems (Fig. 5). The most active catalysts produced higher crystallinity polymers. This fact indicates that, besides a
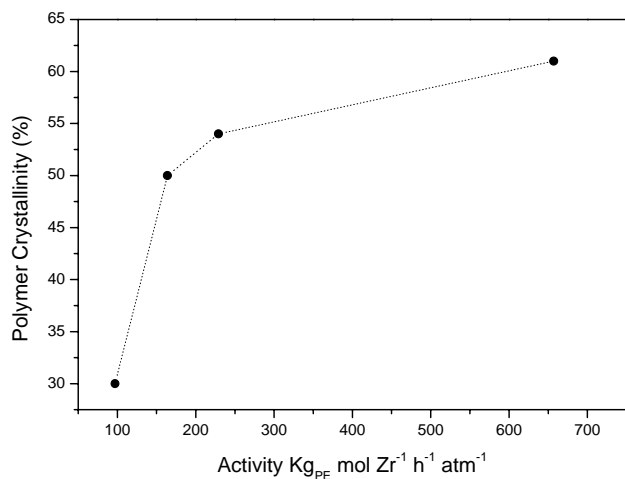
relation of the different immobilization routes on the activity of the synthesized catalysts, these immobilization routes also affected the crystallinity of the materials obtained.

4. Conclusions

Experimental planning results showed that the immobilization route played an important role in the activity of the obtained catalysts. The catalyst synthesized using TMA as modifier agent, in the inverse addition order and impregnation temperature of 60 °C presented the highest activity in ethylene polymerization. Furthermore, all catalysts synthesized using TMA as modifier agent presented higher catalytic activity than those synthesized using MAO.

UV-Vis DRS results suggested the formation of MAO-like species on the silica surface. These species may be formed from the reaction of TMA either with water adsorbed on the support or OH groups of the silica surface. The most active supported catalyst exhibited the most intense absorptive peak related to MAO-like species.

Regarding to the characteristics of the polymers, the polyethylene obtained with the homogeneous phase catalyst presented a different texture when compared with that obtained with the heterogeneous catalyst. The particles of the polyethylene obtained with the heterogeneous catalyst were similar to the silica particles. Furthermore the most active catalysts produced higher crystallinity polymers, indicating a relation of the different immobilization routes on the activity and the crystallinity of the materials obtained.

Fig. 5. Polymer crystallinity vs. supported catalyst activity.

References

[1] R. Quijada, R. Rojas, A. Narvaez, L. Alzamora, J. Retuert, F.M. Rabagliati, Appl. Catal. A: General 166 (1998) 207.

[2] M.R. Ribeiro, A. Deffieux, M.F. Portela, Ind. Eng. Chem. Res. 36 (1997) 1224.

[3] J.H.Z. dos Santos, C. Krug, M.B. da Rosa, F.C. Stedile, J. Dupont, M.C. Forte, J. Mol. Catal. 139 (1999) 199.

[4] J.H.Z. dos Santos, P.P. Greco, F.C. Stedile, J. Dupont, J. Mol. Catal. 154 (2000) 103.

[5] J.H.Z. dos Santos, H.T. Ban, T. Teranishi, T. Uozumi, T. Sano, K. Soga, J. Mol. Catal. 158 (2000) 541.

[6] G.B. Galland, M. Seferin, R. Guimarães, J.A. Rohrmann, F.C. Stedile, J.H.Z. dos Santos, J. Dupont, J. Mol. Catal. 189 (2002) 233.

[7] D. Arrowsmith, W. Kaminsky, A. Schauwienold, U. Weingarten, J. Mol. Catal. 160 (2000) 97.

[8] N.I. Mäkelä-Vaarne, D.G. Nicholson, A.L. Ramstad, J. Mol. Catal. 200 (2003) 323.

[9] F. Ciardelli, A. Altomare, M. Michelotti, Catal. Today 41 (1998) 149.

[10] J.C.W. Chien, D. He, J. Polym. Sci. Part A: Polym. Chem. 29 (1991) 1603.

[11] K. Soga, M. Kaminaka, Makromol. Chem. 194 (1993) 1745.

[12] W. Kaminsky, F. Renner, Makromol. Chem. Rapid Commun. 14 (1993) 239.

[13] Y.X. Chen, M.D. Rausch, J.C. Chien, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 2093.

[14] K. Soga, M. Kaminaka, Makromol. Chem. Rapid Commun. 13 (1992) 221.

[15] R. Quijada, R. Rojas, L. Alzamora, J. Retuert, F.M. Rabagliati, Catal. Lett. 46 (1997) 107.

[16] F.C. Franceschini, T.T.daR. Tavares, P.P. Greco, D. Bianchini, F.C. Stedile, G.B. Galland, J.H.Z. dos Santos, J.B.P. Soares, J. Mol. Catal. 202 (2003) 127.

[17] M. de Fátima, V. Marques, S.C. Moreira, J. Mol. Catal. 192 (2003) 93.

[18] M.C. Haag, C. Krug, J. Dupont, G.B. de Galland, J.H.Z. dos Santos, T. Uozumi, T. Sano, K. Soga, J. Mol. Catal. 169 (2001) 275.

[19] B.A. Krentsel, Y.V. Kissin, V.I. Kleiner, L.L. Stotskaya, Hanser/ Gardner Publications, Cincinnati, 1997, p. 375.

[20] D. Bianchini, K.M. Bichinho, J.H.Z. dos Santos, Polymer 43 (2002) 2937.

[21] J. Scheirs, W. Kaminsky (Eds.), Vol. 1, Wiley, Chichester, UK, 2000, p. 528.

[22] M. Chang, U.S. Patent 5,086,025 (1992).

[23] K.H. Reichet, "Transition Metal Catalyzed Polymerization", Harwood, New York, 1983.