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European Polymer Journal 37 (2001) 1887–1893

EUROPEAN POLYMER JOURNAL

www.elsevier.nl/locate/europolj

Magnesium chloride supported metallocene catalysts in olefin polymerizations

A. Conte, M.F.V. Marques *

Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525, 21945-970 Rio de Janeiro, Brazil

Received 20 March 2000; received in revised form 6 September 2000; accepted 14 March 2001

Abstract

$MgCl_2$ supported systems and homogeneous Cp_2ZrCl_2 and $Et(Flu)_2ZrCl_2$ catalysts were used to investigate their behavior in ethylene and propylene homopolymerization. $MgCl_2$ was activated by vigorous ball milling with ethyl benzoate. Two types of catalysts were prepared: immobilizing the metallocene catalyst directly on the carrier and also immobilizing the metallocene catalyst on the carrier pretreated with methylaluminoxane (MAO). Polymerization was carried out in toluene at 50°C and 60°C. MAO was employed as cocatalyst in all polymerizations. Molecular weight, molecular weight distribution, melting point and crystallinity were determined. It is important to report that the molecular weight distribution of polymers, obtained from $MgCl_2$ supported metallocene catalysts, remained narrow (around 2). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyolefin; Heterogeneous catalyst; Metallocene catalyst; $MgCl_2$ supported catalyst

1. Introduction

Transition metals and organometallics are of great practical and scientific interest as catalyst for olefin polymerization [1–3]. The innovation occurred after the discovery of metallocene/methylaluminoxane (MAO) systems, had revolutionized this field, once this catalyst promises to substitute partial or entirely Ziegler–Natta systems employed in polyolefins industry. At present, research still continues in this area both in catalyst and process developments.

Basically, two types of stereospecific catalysts for olefin polymerization are known: heterogeneous and homogeneous [4–6]. In the first one, stereospecific centers are formed due to the structure in the catalyst crystal lattice (α-, γ-, δ-$TiCl_3$, $TiCl_4/MgCl_2$) [7]. In homogeneous catalytic systems [8], the stereospecificity is related to the steric rigidity of the surrounding ligands and the chirality of active centers.

Despite some rapid developments in the field of metallocene catalysis, it is known that an heterogenation of the soluble compound is necessary [9]. Morphology control of polymer particles represents a major industrial interest. The final form of the polymer product with respect to particle shape, particle size distribution and bulk density, affects the downstream handling and the industrial processing of polymers. The polymer has a tendency to replicate the morphology of the catalyst when polymerization is carried out with some heterogeneous catalyst system.

This study aims to optimize the catalyst productivity by varying the preparation methods to obtain supported metallocene catalyst and through the use of activated $MgCl_2$ as a carrier material.

2. Experimental section

2.1. Chemicals

$MgCl_2$ from Toko, Cp_2ZrCl_2 from Wako Pure Chemical Industry Ltd. and MAO (30 wt.% solution in

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* Corresponding author. Fax: +55-21-270-1317.
E-mail address: fmarques@ima.ufrj.br (M.F.V. Marques).

0014-3057/01/$ - see front matter
PII: S0014-3057(01)00071-4

toluene) from Witco GmbH were used without further purification. Et(Flu)$_2$ZrCl$_2$ was synthesized according to the literature [10].

Nitrogen, used as inert gas, ethylene and propylene were further purified before being used, by sequentially passing them through columns containing 4 Å molecular sieves and copper catalyst as oxygen scavenger. Toluene, before used, was purified by distillation over elemental sodium under nitrogen atmosphere to remove residual traces of moisture and oxygen.

2.2. Support preparation

Anhydrous MgCl$_2$ was brought in contact with ethyl benzoate (EB) (mole ratio $MgCl_2/EB = 0.17$) in a dry box before being submitted to a vigorous ball milling at room temperature for 48 and 110 h in a centrifugal ball mill model S 1000. The characteristics of MgCl$_2$ surface were obtained by nitrogen adsorption at −196°C in a Micromeritics ASAP 2000 apparatus. The pore size (D_p) was calculated from the adsorption isotherm using the BJH model.

2.3. Catalysts preparation

2.3.1. Series S-01 catalyst – MgCl$_2$ treated with the metallocene directly

The milled MgCl$_2$ was introduced under a stream of nitrogen into a schlenk flask coupled with a condenser and a mercury seal. It was treated with 60 ml of Cp$_2$ZrCl$_2$ solution in toluene (0.005–0.54 mmol Zr/g support) or with Et(Flu)$_2$ZrCl$_2$ solution in toluene (0.54 mmol Zr/g support), at 30°C or 110°C for 8 h. The mixture was washed three times with 40 ml of toluene at room temperature and dried under vacuum. A suspension was prepared with the dried catalyst to obtain the following concentration – 0.005 mmol Zr per 2 ml of toluene. This procedure was employed in all the catalysts treatments with Cp$_2$ZrCl$_2$ of Series S-01.

2.3.2. Series S-02 catalyst – MgCl$_2$ pretreated with methyl aluminoxane

Activated MgCl$_2$ was introduced under a stream of nitrogen into a schlenk flask coupled with a mercury seal and was pretreated with MAO ([Al] = 2.5 mmol/g support), in 20 ml of toluene at 50°C for 4 h. The excess of MAO was removed by washing three times with 40 ml of toluene at 70°C. Then the catalyst was treated with the metallocene (Cp$_2$ZrCl$_2$ or Et(Flu)$_2$ZrCl$_2$) in the same way as described for the Series S-01 catalyst. For some catalyst of Series S-02 the support treatment with the metallocene was also performed at room temperature and some catalysts were employed dried in the reaction medium (as can be seen in the following presented tables). This procedure was the same for all catalysts pretreatments with MAO carried out in this study.

2.4. Polymerization procedure

2.4.1. Polymerization in autoclave

Polymerizations were performed in a 0.5 dm^3 doubled walled glass autoclave equipped with vacuum pump and thermotastic bath at 50°C, with 2 bar ethylene overpressure. The stirring speed was 600 rpm. The solvent was introduced into the autoclave. The mixture of 100 ml of toluene, cocatalyst MAO solution (molar ratio $Al/Zr = 2000$) and metallocene catalyst (100 mg) were introduced under nitrogen pressure. Monomer was fed at the polymerization temperature initiating the polymerization. The consumption of monomer was followed using a hot-wire flowmeter (model 5850D) from Brooks Instrument connected to a personal computer through na A/D converter.

The partial pressure of ethylene, and the polymerization temperature were kept constant during the polymerization time.

The polymerization was stopped after 30 min by degassing the reactor, stopping the stirring and adding ethanol containing hydrochloric acid 5%. The obtained polyethylene (PE) was washed with pure ethanol and vacuum dried at 60°C for 12 h.

2.4.2. Polymerization at glass flask

In a 0.25 dm^3 glass flask coupled with a stirrer, 100 ml of toluene, 0.1 M of cocatalyst and metallocene catalyst (100 mg or 0.005 or 0.015 mmol Zr/100 ml of toluene) were introduced into the reactor under a stream of dry nitrogen and then evacuated. Ethylene or propylene was then fed at a constant pressure (1.1 atm). After 1 h reaction time, at 50°C, polymerization was terminated. The isolated polymer was treated in the same way as described for the polymerization in glass autoclave.

2.4.3. Polymer characterization

The molecular weight of the polymer was measured by a Waters 150 CV plus gel permeation chromatograph equipped with a refractive index detector, using a set of polystyrene gel columns and 1-2-4 trichlorobenzene as solvent at 135°C. The number-average and weight-average molecular weight ($\overline{M_n}$ and $\overline{M_w}$ respectively) were calculated on the basis of a polystyrene standard calibration.

The melting temperature (T_m, °C) was measured on a Perkin–Elmer DSC-7 differential scanning calorimeter in the following manner. First, the sample was heated to 180°C at 10°C min^{-1}. The thermogram of each sample was recorded in the second heating run in order to remove the thermal history. The instrument was calibrated by the melting point of indium.

3. Results and discussion

Table 1 lists the characteristics of $MgCl_2$ surface before and after grinding with EB. The surface area, volume and diameter pores enhanced with the increase of grinding time from 48 to 110 h.

Table 2 shows the results of ethylene polymerization using homogeneous and $MgCl_2$ (first grinding) supported metallocene catalysts systems (with and without pretreatment with MAO).

Fig. 1 illustrates the performance of Cp_2ZrCl_2 heterogeneous catalyst systems with different zirconium concentrations in $MgCl_2$ (first grinding), for ethylene polymerizations.

The results obtained in this work suggest that the catalysts prepared with pretreated MAO carrier (Series S-02) are more active than those prepared by direct contact with Cp_2ZrCl_2 (Series S-01).

Therefore, we concluded that the pretreatment with MAO led to an enhancement in the supported catalytic activity, which is related, probably, to the increasing of the amount of active centers fixed. It was also observed that, on the reaction conditions, the catalytic activity increased for the catalysts prepared until 0.40 mmol Zr/g support.

Table 1
Characteristics of $MgCl_2$ after first and second grinding

	Before grinding	First grinding (48 h)	Second grinding (110 h)
Surface area (m^2/g)	2.26	48.7	53.9
Pores volume[a] (cm^3/g)	0.008	0.250	0.328
Pores diameter (Å)	56	129	159

[a] By cumulative adsorption between 20 and 3000×10^6 Å.

The analysis results of some heterogeneous catalysts, by spectrometry of plasma emission, illustrated in the Table 3, indicate that the zirconium concentration fixed in the Series S-02 catalyst was higher than that one fixed in Series S-01 catalyst. The role of MAO in stabling the active centers on the support surface must be also considered, once it was observed an increase in the molecular weight in comparison to the Series S-01 catalyst correspondent.

Furthermore, our results showed that the $MgCl_2$-based heterogeneous catalyst system produced PE with higher molecular weights and melting points when compared with the one obtained with the homogeneous precursor.

Table 4 and Fig. 2 present data of ethylene homopolymerizations with Cp_2ZrCl_2 supported catalyst (Series S-02) on $MgCl_2$ (first and second grinding) at 30°C and 110°C, and also $Et(Flu)_2ZrCl_2$ heterogeneous catalyst (Series S-02) supported on $MgCl_2$ (second grinding) at 30°C.

The present observations show that on decreasing the Cp_2ZrCl_2 impregnation temperature on the carrier (0.54 mmol Zr/g support) from 110°C to 30°C, higher PE yields are achieved. High temperature enhances the entropy of the system and also hinder the Zr fixation on the carrier surface. In conclusion, the Zr fixation on the carrier surface is due mostly to physic adsorption. The catalytic activity enhanced with increasing the grinding time of the carrier from 48 to 110 h. This was because of the rise in the surface area and consequently, in the amount of active sites on the support.

By supporting $Et(Flu)_2ZrCl_2$ catalyst on $MgCl_2$ pretreated with MAO we observed lower activity in comparison with Cp_2ZrCl_2 heterogeneous catalyst system. This was attributed to the $Et(Flu)_2ZrCl_2$ molecule size, which is a very voluminous complex and for this reason, is not easily adsorbed by the carrier.

$MgCl_2$ (first and second grinding) supported at 110°C (Series S-02) and homogeneous Cp_2ZrCl_2 catalyst

Table 2
Ethylene polymerization using Cp_2ZrCl_2 homogeneous and $MgCl_2$ (first grinding) supported catalyst systems

mmol Zr/g support	Catalyst series	Yield (g)	Catalytic activity (g PE/g cat)	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	T_m (°C)	Crystallinity (%)
0.10	S-01	5.21	104.6	1.59	2.0	138.2	58.4
	S-02	7.48	149.6	2.71	2.0	137.5	47.1
0.30	S-01	3.39	203.0	nd	nd	140.3	55.1
	S-02	4.65	278.4	4.11	1.9	137.3	62.4
0.40	S-02	4.50	360.0	6.60	2.4	139.9	57.2
–	Homogen	12.26	–	1.09	2.5	133.7	65.5

Polymerization conditions: temperature – 60°C, reaction time – 1 h, volume of toluene – 100 ml, [Zr] = 0.005 mmol, cocatalyst concentration – 0.1 M, ethylene pressure – 1.1 atm.

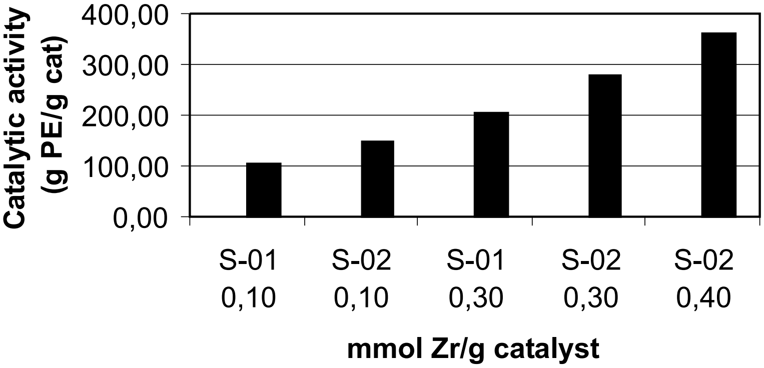

Fig. 1. Influence of zirconium concentration employed in the $MgCl_2$ treatment on the ethylene polymerizations.

Table 3
Zr content fixed onto $MgCl_2$ surface after Cp_2ZrCl_2 metallocene catalyst impregnation at 110°C

Zr content added (mmol Zr/g support)	Catalyst series	Zr content fixed (mmol Zr/g support)
0.05	S-01	0.0030
	S-02	0.0180
0.10	S-01	0.0016
	S-02	0.0081
0.30	S-01	0.0016
	S-02	0.0046

performance in ethylene homopolymerization carried out in glass autoclave is reported in Table 5.

According to the results showed in Table 5, Cp_2ZrCl_2 and also $Et(Flu)_2ZrCl_2$ supported systems polymerized ethylene with higher molecular weight compared to the homogeneous precursors.

In Figs. 3 and 4 are plotted the results of $MgCl_2$ (Series S-02) heterogeneous Cp_2ZrCl_2 catalyst in ethylene homopolymerization performed in glass autoclave. In order to compare the data obtained with the supported catalyst system, rate time plot for the $Et(Flu)_2$-$ZrCl_2$ homogeneous catalyst system is included.

Accordingly, catalysts prepared with longest time of $MgCl_2$ grinding had an improvement in the efficiency in relation to the catalyst prepared with $MgCl_2$ milled for 48 h. This means that the increase in the support surface area enhanced, after Cp_2ZrCl_2 impregnation, the amount of active centers.

Kinetic profiles of heterogeneous catalysts and of homogeneous analogues are alike, so we conclude these catalysts have similar active centers.

Table 6 shows the productivity of propylene homopolymerizations with heterogeneous and homogeneous Cp_2ZrCl_2 catalyst systems.

The results showed that, unlike PE synthesis, catalytic activity was also growing with the enhancement of Zr content added in the carrier surface, which is due to the increase in the amount of active sites. These heterogeneous catalysts have no stereoregularity, so the polypropylene obtained has no crystallinity.

Table 4
Ethylene polymerization: homogeneous and $MgCl_2$ (first and second grinding) supported Cp_2ZrCl_2 and $Et(Flu)_2ZrCl_2$ catalysts systems

Catalyst	mmol Zr/g support	Catalyst series	Yield (g)	Catalytic activity (g PE/g cat)	$\overline{M_w} \times 10^{-5}$	$\overline{M_w}/\overline{M_n}$
Cp_2ZrCl_2	0.54	S-02[a]	6.00	60.0	2.02	3.5
	0.54	S-02[b]	10.23	102.3	0.89	2.1
	0.54	**S-02**[a]	**9.13**	**91.3**	**1.52**	**2.5**
Cp_2ZrCl_2	–	Homogene	12.26	–	1.09	2.5
$Et(Flu)_2ZrCl_2$	**0.54**	**S-02**[a]	**0.60**	**6.0**	**6.91**	**2.2**

Polymerization conditions: amount of catalyst – 100 mg, temperature – 60°C, reaction time – 1 h, volume of toluene – 100 ml, cocatalyst concentration – 0.1 M, ethylene pressure – 1.1 atm. Bold indicates the Zr grafting at 30°C.

[a] $MgCl_2$ of first grinding.

[b] $MgCl_2$ of second grinding.

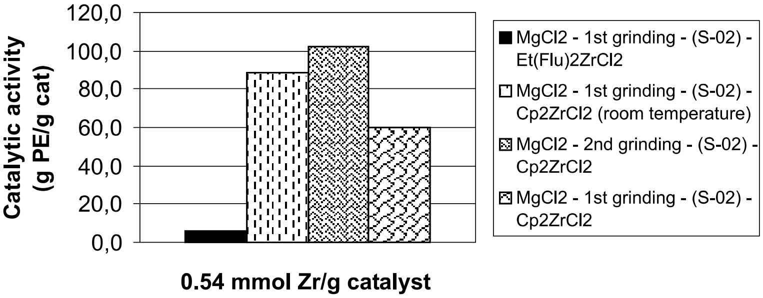

Fig. 2. Performance of Cp_2ZrCl_2 and $Et(Flu)_2ZrCl_2$ heterogeneous catalysts systems: effect of carrier time grinding and zirconocene temperature grafting reaction on the catalytic activity for ethylene homopolymerizations.

Table 5
Results of ethylene homopolymerization in glass autoclave: $MgCl_2$ (first and second grinding) heterogeneous and homogeneous Cp_2ZrCl_2 and $Et(Flu)_2ZrCl_2$

Catalyst	mmol Zr/g support	Catalyst series	Yield (g)	Catalytic activity (g PE/g cat)	$\overline{M_w} \times 10^{-5}$	$\overline{M_w}/\overline{M_n}$
Cp_2ZrCl_2	0.54	S-02[a]	4.23	42.3	5.63	2.7
	0.54	S-02[b]	7.86	78.6	3.96	2.7
Cp_2ZrCl_2	–	Homogene	4.26	–	1.40	2.2
$Et(Flu)_2ZrCl_2$	0.54	S-02	0.45	4.5	12.98	1.5
$Et(Flu)_2ZrCl_2$	–	Homogene	3.50	–	6.64	2.4

Polymerization conditions: amount of catalyst – 100 mg, temperature – 50°C, reaction time – 30 min, volume of toluene – 100 ml, cocatalyst concentration – 0.1 M, ethylene pressure – 2 bar.

[a] $MgCl_2$ of first grinding.

[b] $MgCl_2$ of second grinding.

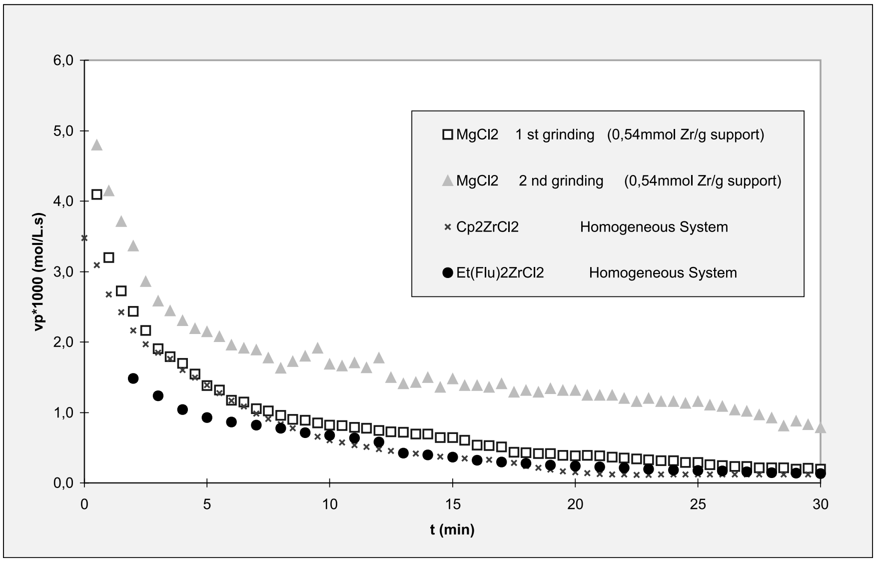

Fig. 3. Effect of $MgCl_2$ activation time on kinetic profiles of Cp_2ZrCl_2/MAO heterogeneous catalytic system (Series S-02) for ethylene homopolymerization.

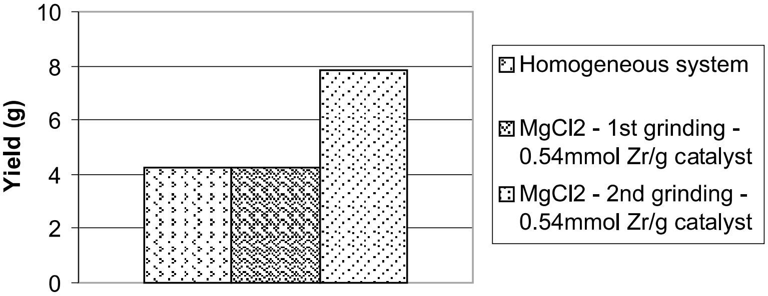

Fig. 4. Effect of $MgCl_2$ activation time in the productivity of Cp_2ZrCl_2/MAO heterogeneous catalytic system (Series S-02) for ethylene homopolymerization.

Table 6
Propylene homopolymerization: $MgCl_2$ (first grinding) supported Cp_2ZrCl_2 catalyst

mmol Zr/g support	Catalyst series	Yield (g)	Catalytic activity (g PP/g cat)
0.10	S-01	3.51	23.4
	S-02	3.30	22.0
0.15	S-01	4.54	45.4
–	Homogene	4.55	–

Polymerization conditions: temperature – 60°C, reaction time – 1 h, volume of toluene – 100 ml, [Zr] = 0.015 mmol, propylene pressure – 1.1 atm.

Fig. 5. Homogeneous system (30×).

Morphological investigations were performed on micrographies of polyethylene with $MgCl_2$ heterogeneous and homogeneous metallocene catalyst and showed in Figs. 5 and 6, respectively.

The micrographies showed that the PE obtained from homogeneous catalyst system have lower particle size and large range of sizes.

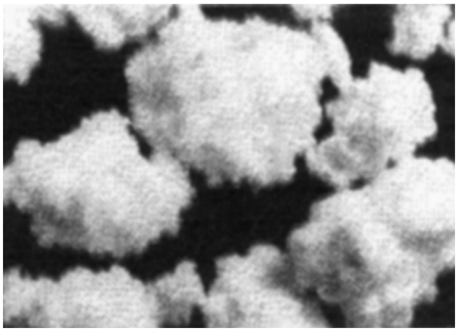

Fig. 6. Supported catalyst (20×).

Besides, PE produced with $MgCl_2$ supported Cp_2ZrCl_2 catalyst system are greater and homogeneous particles.

4. Conclusion

1. Immobilizing the Cp_2ZrCl_2 catalyst on MAO pretreated $MgCl_2$ higher activity was obtained in comparison with the catalyst on which no pretreatment was performed.
2. The voluminous complex $Et(Flu)_2ZrCl_2$ supported on $MgCl_2$ showed very low activity in relation to the heterogeneous Cp_2ZrCl_2 catalyst showing the difficulties in supporting higher molecular weight metallocenes on solid materials.
3. The improvement in the Cp_2ZrCl_2 amount used in the carrier treatment (until 0.40 mmol Zr/g support) enhanced the catalytic activity.
4. $MgCl_2$ activated for 110 h and the carrier treatment with Cp_2ZrCl_2 at 30°C produced the most reactive catalytic system.

5. The kinetic profiles of $MgCl_2$ supported metallocene catalyst systems were very similar to that of homogeneous analogues.
6. $MgCl_2$ seemed to be an appropriate carrier to the heterogenization of metallocene catalysts.

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