

# The Influence of the Preparing Conditions of SiO<sub>2</sub> Supported Cp<sub>2</sub>ZrCl<sub>2</sub> Catalyst on Ethylene Polymerization

Maria de Fátima V. Marques, Anunciata Conte

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

Received 23 January 2001; accepted 25 February 2002

**ABSTRACT:** In this work, ethylene was polymerized by using Cp<sub>2</sub>ZrCl<sub>2</sub> supported on silica pretreated with methylaluminoxane (MAO) as the catalyst system. The influence of the conditions for the preparation of the heterogeneous catalyst, such as temperature, washing method of the catalytic solid, MAO and metallocene concentration in the support treatment, time of MAO, and metallocene immobilization on the support, type of alkylaluminum used in the support pretreatment, and calcination temperature of the support were investigated. Aluminum and zirconium content fixed on the silica surface were determined by inductively coupled plasma emission spectroscopy. Polymer characteristics

were determined by gel permeation chromatography and differential scanning calorimetry. According to the results, the activity of some supported catalysts were far higher than with the homogeneous system. Moreover, polyethylene with very high molecular weights were also obtained and with molecular weight distribution larger than those produced with the homogeneous precursor. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2054–2061, 2002

**Key words:** metallocene; supported catalyst; polyethylene; methylaluminoxane; silica

## INTRODUCTION

The discovery of metallocene/methylaluminoxane (MAO) catalysts has been one of the most exciting developments in recent times. Metallocene compound, when combined with MAO or other suitable cocatalysts, polymerize olefins with extremely high activities.<sup>1</sup> Metallocenes are single-site catalysts and differ from conventional olefin polymerization systems in that the metal atom is in a constrained environment that allows single access by monomers to the active site.

Because of this single-site geometry, great control can be exercised over the microstructure of the produced polymer, and consequently, metallocene catalysts exhibit several advantages, such as the capability to produce extremely uniform polymers (i.e., the degree of regularity, molecular weight, and composition fall in very narrow ranges). Also, it is very important to notice that, by investigating the route and kinetics of the chain growth, a polymer can be designed for a particular performance target.

The use of the metallocenes as homogeneous catalysts is, however, of no applicability in both slurry and gas-phase processes and, therefore, they also lack the ability of controlling polymer morphology, such as

particle shape and size, bulk density, etc. Moreover, another negative point of these systems is the large excess of MAO required for the metallocene to have high catalytic activity. Besides, MAOs also have other drawbacks such as high cost, due to the expensive AlMe<sub>3</sub> parent compound, and because of the large amount needed, there is a high amount of aluminum residual in the final product.<sup>2</sup>

To overcome these difficulties, much effort was made to modify the metallocene ligands as well as to develop active heterogeneous metallocene catalysts. A large variety of solid materials were studied as support for the metallocene compounds, and some of them are magnesium dichloride, silica, alumina, zeolites (inorganic solids), or polymers (organic solids), etc. Magnesium dichloride was the best support for the conventional Ziegler–Natta catalyst, which is considered the fourth generation catalyst.<sup>3,4</sup> In addition, when the metallocenes are supported on magnesium dichloride, high catalytic activity is achieved,<sup>4–6</sup> and also, in general, polymers with broad polydispersion are produced, indicating a multiplicity of active sites.<sup>7</sup> Alumina is an inorganic oxide studied often as support for the metallocene catalysts and  $\gamma$ -alumina is the type that is most frequently used.<sup>8–12</sup> Furthermore, as silica is available in a large range of particle size and pore-size distribution and, because of these ranges can be controlled during its synthesis, this solid material is also one of the inorganic oxides that is greatly explored in research as support for the metallocene catalysts.<sup>7–10,12–22</sup>

Correspondence to: M. d. F. V. Marques (fmarques@ima.ufrj.br).

Heterogenization of metallocene catalysts offer several advantages, as follows: preserving fairly high activity and the features such as single-site, narrow comonomer, and molecular weight distributions, and high ability to incorporate comonomers as with unsupported metallocenes; capacity of controlling the morphology of the polymer to reduce the possibility of reactor fouling; and adaptation to a gas-phase process.

The present investigation is concerned with supporting  $\text{Cp}_2\text{ZrCl}_2$  on silica by using different preparation methods to find a more reactive catalyst for ethylene polymerization.

## EXPERIMENTAL

### Chemicals

Nitrogen, used as inert gas, and ethylene were purified by sequentially passing them through columns containing 4 Å molecular sieves and copper catalyst.

Toluene, before use, was purified by distillation over elemental sodium under nitrogen atmosphere to remove residual traces of moisture and oxygen.

Commercial silica gel (Grace Davison, Sylopol 948), with a surface area of 309 m<sup>2</sup>/g, was used as support after calcination under inert gas.

$\text{Cp}_2\text{ZrCl}_2$  from Wako Pure Chemical Industry, Ltd. and trimethylaluminum (TMA) (15 wt % solution in toluene) and MAO (10 wt % solution in toluene) from Witco GmbH were used without further purification.

### Support preparation

Silica gel was calcinated at 400 or 200°C for 4 h under nitrogen atmosphere before being allowed to react with MAO and the metallocene compound.

### Catalyst preparation

All the reactions were performed under nitrogen atmosphere by using a standard Schlenk technique.

At first, the influence of MAO and  $\text{Cp}_2\text{ZrCl}_2$  concentration or the metallocene immobilization temperature on the preparation of the heterogeneous catalyst was evaluated (Table I).

Taking into account the results obtained in the first set of experiments, further studies were conducted and the catalyst performances were compared.

In the second part of this study, supported catalysts were prepared by allowing the metallocene compound to react with silica in toluene, basically in the following way:

1. Calcinating silica at 400 or 200°C and without chemical modification;

**TABLE I**  
Variables Studied in the First Experimental Set

Supported catalyst	$T_{\text{immobilization}} \text{Cp}_2\text{ZrCl}_2$ (°C)	[MAO] 0–5 mmol Al/g silica	$[\text{Cp}_2\text{ZrCl}_2]$ 0.05–0.50 mmol Zr/g silica
R1	70	2.5	0.275
R2	70	2.5	0.275
R3	70	2.5	0.275
Cat1	110	0	0.050
Cat2	110	0	0.500
Cat3	110	5.0	0.050
Cat4	110	5.0	0.500
Cat5	30	0	0.050
Cat6	30	0	0.500
Cat7	30	5.0	0.050
Cat8	30	5.0	0.500

2. Pretreating the calcinated silica with MAO or TMA (5 or 10 mmol Al/g silica) for 4 or 8 h;
3. Removing the excess of alkylaluminum by washing the support three times with 40 mL of toluene, at 90°C or environmental temperature, in a Schlenk filter;
4. Immobilizing the  $\text{Cp}_2\text{ZrCl}_2$  on the pretreated silica (0.05 mmol Zr/g silica) at 110°C, for 4 or 8 h;
5. Evaporating the suspension solvent, only for cat A5;
6. Washing the catalyst three times with 40 mL of toluene in a Schlenk filter and, finally, drying it under vacuum.

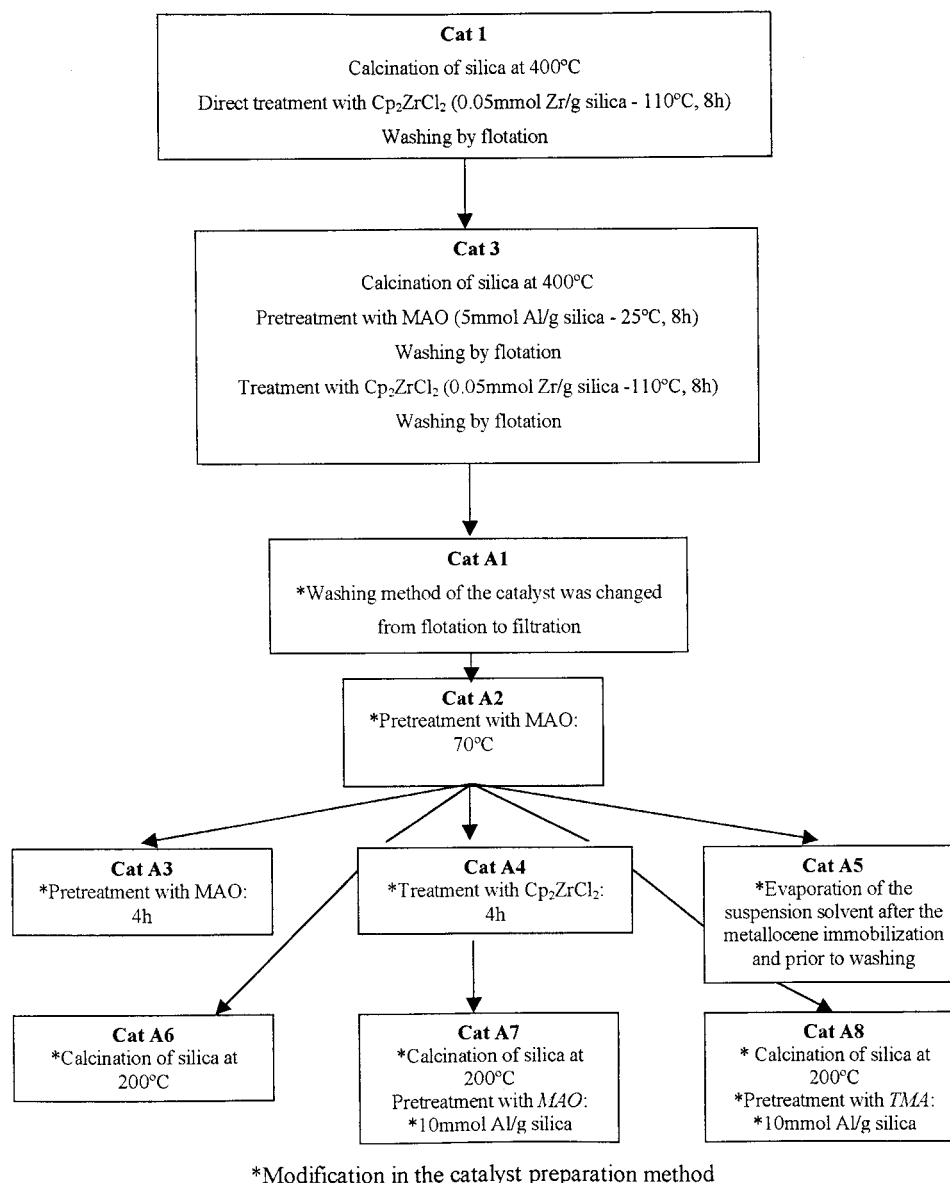
Schematic representation of the different preparation methods described above for the heterogeneous catalysts prepared in the second part of this work is presented in Figure 1.

### Catalyst characterization

Aluminum and zirconium contents fixed on the catalyst surface were determined by inductively coupled plasma (ICP) emission spectroscopy. The sample was treated with chloridic, nitric, fluoridic, and perchloric acids and heated by using a microwave oven. A solution was prepared in a volumetric flask and the contents were determined in a Perkin–Elmer 2000, calibrated with standard solutions containing known amounts of the same concentration magnitude of the analyzed solutions. Each catalyst sample was analyzed in duplicate with two readings per analysis and the variation coefficient of the results was <5%.

### Ethylene polymerization

Into a 250-mL round-bottom glass flask, equipped with a mechanical stirrer and gas inlets, 100 mL toluene, 0.01M MAO solution, and 100 mg of the hetero-



**Figure 1** Preparation methods of the heterogeneous catalysts.

geneous catalyst or 0.005 mmol of the metallocene compound in toluene were introduced. Polymerization of ethylene was carried out at 50°C, 1 h, and 1.1 atm of monomer pressure. All supported catalysts were kept in contact with the MAO for 3 min under vigorous stirring and nitrogen atmosphere before starting the polymerization reaction. To interrupt the reaction, monomer feed was stopped and acidified ethanol was added. The obtained polymers were filtered, washed with ethanol, and dried under vacuum at 60°C to constant weight.

### Polymer characterization

Weight-average molecular weight ( $\bar{M}_w$ ) and molecular weight distribution ( $\bar{M}_w/\bar{M}_n$ ) were determined in

1,2,4-trichlorobenzene by SEC (Waters 150CV plus) at 135°C calibrated with polystyrene standards. Melting crystallization behavior of the polymers was examined by using a Perkin-Elmer differential scanning calorimeter DSC-7. Three runs (first heating, cooling, second heating) were performed at a heating rate of 10°/min in the temperature range of 30–190°C. The second heating–melting peak temperature was taken as a melting point.

### RESULTS AND DISCUSSION

Zirconium and aluminum contents fixed on silica surface of the heterogeneous catalysts prepared in the first study are presented in Table II.

TABLE II  
Zirconium and Aluminium Content Added and Fixed on the Silica

Supported catalyst	$\text{Al}_{\text{added}}$ (mmol/gsilica)	$\text{Al}_{\text{fixed}}$ (mmol/gsilica)	$\text{Zr}_{\text{added}}$ (mmol/gsilica)	$\text{Zr}_{\text{fixed}}$ (mmol/gsilica)	$\text{Zr}_{\text{fixed}}$ (%)
R1	2.5	2.30	0.275	0.121	44
R2	2.5	1.85	0.275	0.143	52
R3	2.5	1.89	0.275	0.143	52
1	0	0.04	0.050	0.027	54
2	0	0.01	0.500	0.274	55
3	5.0	3.71	0.050	0.021	42
4	5.0	4.26	0.500	0.126	25
5	0	0.01	0.050	0.024	48
6	0	0.04	0.500	0.077	15
7	5.0	3.97	0.050	0.021	42
8	5.0	3.15	0.500	0.102	20

Figure 2 shows the influence of the catalyst preparing conditions on the zirconium content fixed on the support of the first experimental set.

When 0.050 mmol Zr/g silica was employed in the catalyst preparation, the different conditions studied in the immobilization of the metallocene did not significantly affect the Zr content fixed on the support, and values slightly higher than 0.020 mmol Zr/g silica were fixed. This means that about 45% of the metallocene complex was immobilized on the catalytic solid. This value was higher (55%) when the immobilization reaction was conducted at 110°C and slightly lower when the support was pretreated with MAO. According to the literature,<sup>23</sup> this was probably due to the decrease in the pore volume of silica pretreated with MAO. Another hypothesis should be the partial leaching of the Zr compound added over the MAO fixed on silica surface caused by exhaustive washing with toluene. On the other hand, at 0.500 mmol Zr/g silica and 110°C, a great enhancement on the Zr content fixed on silica was observed, especially when the support was not pretreated with MAO. These results showed that to achieve high amounts of zirconium fixed on the support surface, the conditions to be employed should be a high temperature of Zr immobilization and high concentration of the metallocene compound added directly to silica, without pretreatment with MAO.

The influence of the variables studied on the catalytic performance and polyethylene characteristics are shown in Table III.

The results showed that the variable that most negatively influenced the catalytic activity was the increase of the metallocene concentration; moreover, the increase in the metallocene immobilization temperature also contributed to diminish the catalytic activity. On the other hand, the increase on MAO concentration on the pretreatment of silica promoted an enhancement of the catalytic activity. These results indicate that, even decreasing the amount of Zr fixed on the support, the presence of MAO seems to stabilize

the active center and preserve the catalytic activity. Besides, the catalytic activity is only enhanced by the increase in the metallocene concentration and also the immobilization temperature when MAO concentration is increased concomitantly.

It is very important to highlight that some catalysts produced activities strongly higher than the homogeneous precursor, showing that the heterogenization decreased the bimolecular deactivation reaction, a very common action on the part of the homogeneous metallocene systems.

In Figure 3, the catalytic activity of the homogeneous  $\text{Cp}_2\text{ZrCl}_2$  and support on silica are compared.

The results showed that the increase of Zr concentration added to the catalyst preparation promoted an enhancement on Zr content fixed on the support, although the activity decreased considerably. It is believed that bimolecular deactivation of the metallocene compound occurred during the support treatment and than inactive bimetallic species were fixed.<sup>24</sup> Heterogeneous systems with similar Zr content fixed on the support presented different catalytic activity due to the different catalysts preparing conditions such as support pretreatment and  $\text{Cp}_2\text{ZrCl}_2$  immobilization temperature. These results are better illustrated in Figure 4 and the influence of the Zr content fixed over the support on the catalytic activity (ton PE/mol Zr h) is shown.

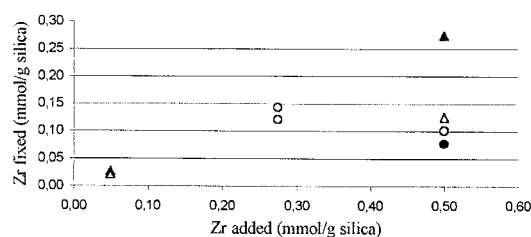


Figure 2 Zr content fixed  $\times$  Zr content added.

TABLE III  
Results of Ethylene Polymerization

Cat.	Yield (g)	$M_w \times 10^{-5}$	$M_w/M_n$	$T_m$ (°C)	$X_c$ (%)	Productivity (gPE/gcat h)	Catalytic activity (tonPE/molZr h)
R1	14.66	1.11	3.5	131.8	74	146.6	1.21
R2	14.52	1.32	3.6	131.8	74	145.2	1.02
R3	14.03	1.00	3.7	131.5	75	140.3	0.98
Cat 1	9.67	3.20	3.4	133.2	64	96.7	3.58
Cat 2	11.17	1.16	4.1	131.0	75	111.7	0.41
Cat 3	17.62	2.22	3.7	133.3	72	176.2	8.39
Cat 4	16.32	1.55	3.9	132.2	73	163.2	1.30
Cat 5	16.01	2.96	3.3	133.5	67	160.1	6.67
Cat 6	14.65	1.90	3.6	132.6	71	146.5	1.90
Cat 7	13.89	2.30	3.7	133.0	70	138.9	6.61
Cat 8	14.47	1.52	3.9	132.2	74	144.7	1.42
H*	10.9	1.46	2.0	131.0	65	—	2.18

Polymerization conditions: 100 mL toluene, 0.01M MAO, 100 mg of catalyst or 0.005 mmol Zr, 50°C; 1.1 atm of ethylene; 1 h. H\*, homogeneous system.

Concentrations  $< 0.005$  mmol Zr/g support were not employed in this study. Moreover, below a determined value of zirconocene concentration, the activity will surely decrease once the number of the active centers decrease, although a lower number of bimolecular deactivation reaction would occur.

The initial results also showed that the molecular weight of the polyethylene obtained by the catalysts containing higher Zr content fixed was always lower, with the support pretreated or not with MAO. It is believed that the supported catalysts are formed by isolated and vicinal active centers and that the latter, at higher concentration when the Zr content fixed increases, are responsible for the decrease of the polyethylene molecular weight.

The polydispersion of the polyethylene produced did not vary with the different methods of preparing the supported catalysts and is considered to be broadened in comparison to that of polyethylene obtained with the homogeneous system ( $M_w/M_n = 2.0$ ). Then, it is possible that different kinds of active centers are acting simultaneously, which could be the isolated and the vicinal active centers. On the other hand, the

crystallinity and the melting temperature of the produced polymers were not influenced by any of the parameters evaluated in the study and were similar to the one obtained with the homogeneous system.

It is very important to mention that these results can be applied for metallocene catalysts such as  $Cp_2ZrCl_2$ . For more voluminous complexes, such as systems with indenyl or fluorenyl, the conditions for the preparation of catalysts with very high activities can be very different, as was already observed by our research group.

Figure 4 clearly shows that the most important factor for the preparation of the heterogeneous catalysts to obtain high activity is not the Zr content fixed on the catalyst surface but how much of the Zr is effectively active.

On the second step of this work and according to experiments established in Figure 1, a new set of supported catalysts (A1 to A8) were prepared and the results of ethylene polymerization are presented in Table IV. For comparison, the performance of catalysts 1 and 3 of the first experimental planning were also presented. Higher catalytic activity (ton PE/mol Zr h) regarding to the homogeneous precursor was also

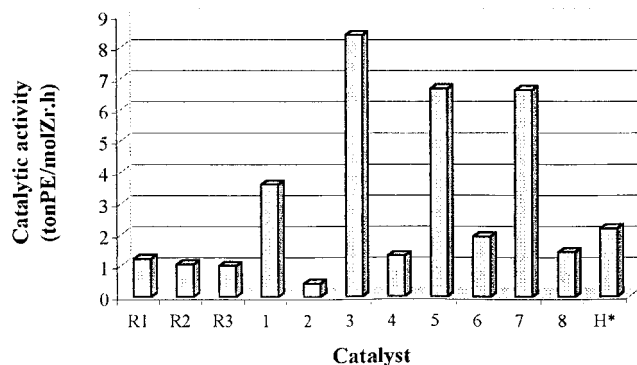


Figure 3  $Cp_2ZrCl_2$  homogeneous system and supported on silica under different conditions.

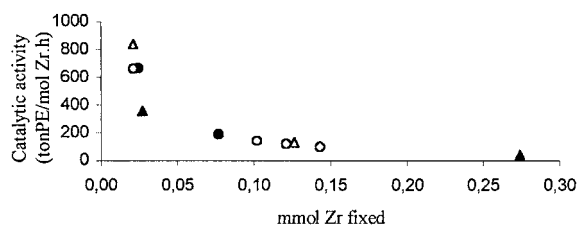


Figure 4 Influence of the Zr content fixed on silica on the catalytic activity.

TABLE IV  
Results of Ethylene Polymerization

Cat.	$\text{Al}_{\text{added}}$ (mmol/ gsilica)	$\text{Al}_{\text{fixed}}$ (mmol/ gsilica)	$\text{Zr}_{\text{fixed}}$ (mmol/ gsilica)	Productivity (gPE/gcat h)	Catalyst activity (tonPE/molZr h)	$M_w \times 10^{-5}$	$M_w/M_n$	$T_m$ (°C)	$X_c$ (%)
1	0	0.05	0.027	110.1	4.08	4.22	3.5	133.0	62
3	5	3.71	0.021	176.2	8.39	2.22	3.7	133.3	72
A1	5	3.41	0.037	60.6	1.64	7.91	2.7	135.6	70
A2	5	3.63	0.046	68.5	1.49	1.05	3.5	131.3	69
A3	5	3.45	0.036	46.2	1.28	8.18	2.8	135.4	48
A4	5	3.11	0.036	39.1	1.09	8.58	2.5	135.3	45
A5	5	3.48	0.041	77.3	1.89	6.50	3.1	135.9	50
A6	5	3.04	0.029	30.6	1.06	6.44	3.5	134.2	51
A7	10	3.15	0.029	68.8	2.37	5.30	2.7	134.2	51
A8	10	0.88	0.022	56.7	2.58	7.36	2.9	nd	nd
H*	—	—	—	—	2.18	1.46	2.0	131	65

Polymerization conditions: 100 toluene, 0.01M of MAO, 100 mg catalyst or 0.005 mmol Zr, 50°C, 1.1 atm of ethylene, 1 h. H\*, homogeneous system.

achieved by these supported systems. For better comprehension, Figure 5 illustrates the results obtained in relation to the catalyst characterization and activity.

Figure 5 shows that, in the studied range, the zirconium amount fixed on the solid surface was more influenced by the conditions of the catalyst preparation than the amount of aluminum fixed.

Now, it was amazing to find that by changing the washing method from flotation to filtration the catalyst activity has sharply diminished, despite the higher amount of fixed zirconium on the support. This indicates that the majority of the zirconium fixed on silica was inactive for ethylene polymerization. In the flotation washing method, the contact time between the solvent and the catalyst was higher and was performed under vigorous stirring; consequently, the washing was more efficient and allowed the elimination of more inactive than active zirconium species. The inactive species may be the voluminous bimetallic

zirconium species formed during the immobilization of  $\text{Cp}_2\text{ZrCl}_2$ .

Figure 6 presents the weight-average molecular weight, polydispersion, and catalyst activity obtained with silica supported and homogeneous  $\text{Cp}_2\text{ZrCl}_2$  catalysts in ethylene polymerization.

In general, the weight-average molecular weights of the produced polyethylene with catalysts from A1 to A8 are much higher and the polydispersion narrower when compared to the one obtained with cat 3. These facts may be related to the polymerization heat development, which could not be immediately dispersed in the reaction medium by very active catalyst (cat 3), and then caused chain transfer reactions decreasing the polymer molecular weight, but also to the less diversity of active sites of the former catalysts, respectively.

Cat A2 was prepared by employing a higher temperature in the MAO support pretreatment. This pre-

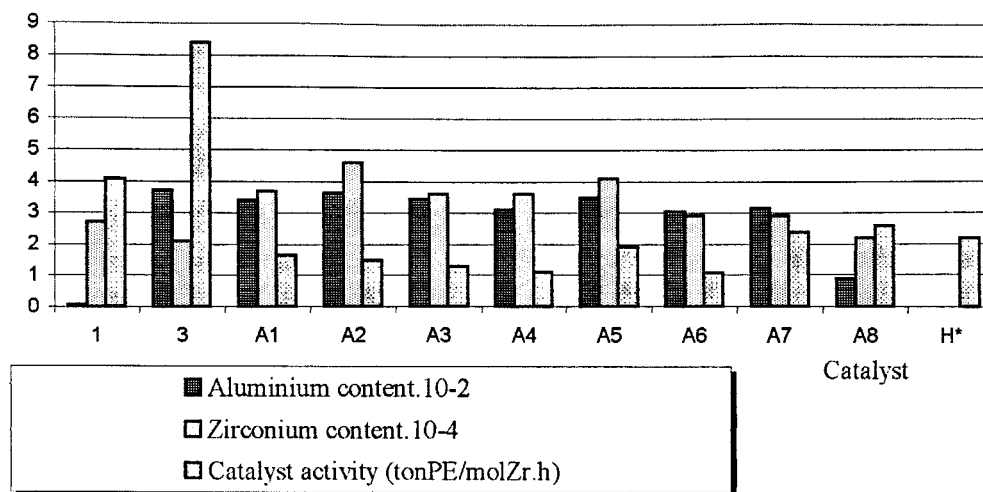
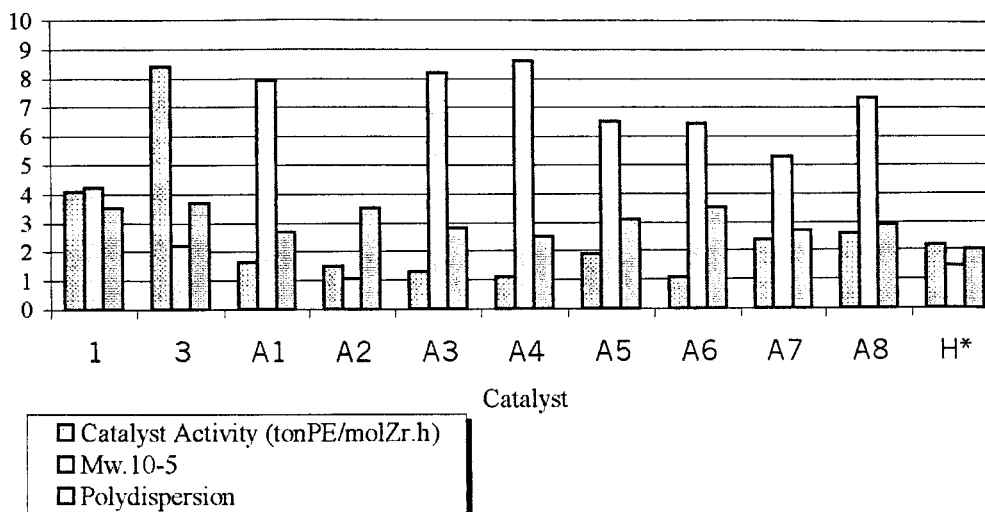


Figure 5 Catalyst activity, aluminum, and zirconium content fixed on the support.



### H\* - Homogeneous system

**Figure 6** Weight-average molecular weight and polydispersion of the obtained polyethylene and catalyst activity.

paring condition slightly enhanced the aluminum content and consequently the zirconium amount on the catalyst surface.

As we can see in Figure 6, cat A2 produced polyethylene with low weight-average molecular weight. One very important point is that, as previously mentioned in the literature, some heterogeneous catalysts pretreated with MAO produced polymers with similar characteristics to the homogeneous metallocenes precursors. That would be due to the migration of the metallocene compound through the MAO fixed on the support, producing a system with similar mobility to the homogeneous.<sup>7</sup> In the first experimental planning, it was observed that the polyethylene produced with catalysts pretreated or not with MAO, but with greater amounts of zirconocene, showed higher weight-average molecular weight.

On the other hand, by decreasing the time of MAO pretreatment, a lower amount of aluminum was fixed and less active catalyst (cat A3) was obtained. Moreover, diminishing the time of  $\text{Cp}_2\text{ZrCl}_2$  immobilization from 8 to 4 h (cat A4), the activity was also decreased.

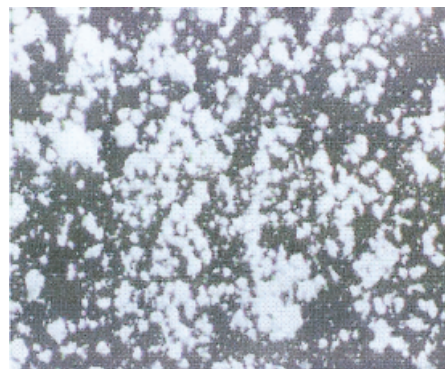
Among all the new preparation conditions, the most active catalyst was prepared when the solvent was taken away from the  $\text{Cp}_2\text{ZrCl}_2$  and support suspension after 8 h of contact time prior to washing (cat A5). This means that, by using this method, the adsorption was forced by the continuous increase in the  $\text{Cp}_2\text{ZrCl}_2$  concentration during evaporation, resulting in higher zirconium content on the support.

Cat A6 was prepared from a silica calcinated at 200°C instead of 400°C, which means there were more hydroxyl groups on its support surface. The catalytic activity of cat A6 was lower, probably because part of MAO reacted with vicinal OH groups and had not

been fixed on the support surface, being washed after its treatment and consequently, fixing less zirconium amount. By using a higher MAO concentration (cat A7), the catalyst activity sharply increased, compensating the presence of such OH groups.

The last treatment used TMA instead of MAO in the support pretreatment before the immobilization of  $\text{Cp}_2\text{ZrCl}_2$ . The amount of zirconium species on the support treated with TMA was lower than that when MAO was first fixed, and also lower was the catalyst activity, indicating that MAO acts to capture and stabilize  $\text{Cp}_2\text{ZrCl}_2$  molecules.

Figures 7-9 show the micrographs of polyethylenes produced by using  $\text{Cp}_2\text{ZrCl}_2$  in the homogeneous system, supported on silica prepared by washing the catalyst by flotation (cat A), and supported on silica prepared by washing the catalyst by filtration (cat B), respectively. The micrographs show very clearly the increase in the polymer particle size, probably due to the enhancement on the weight-average molecular



**Figure 7** Polyethylene obtained with homogeneous system ( $\times 30$ ).

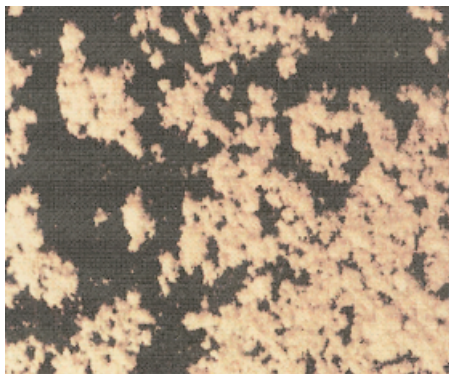


Figure 8 Polyethylene obtained with cat A ( $\times 30$ ).

weight of the resin and, consequently, to the entanglements of the polymer chains, when the metallocene is supported on silica (cat B, Fig. 9) in comparison to the homogeneous system (Fig. 7) and supported cat A (Fig. 8).

### CONCLUSION

The preparation method of the supported catalyst may give rise to completely different catalyst systems and also to polymers with varied characteristics.

Enhancing the temperature of MAO support pretreatment from room temperature to  $70^\circ\text{C}$ , and evaporating the  $\text{Cp}_2\text{ZrCl}_2$  solution after its immobilization



Figure 9 Polyethylene obtained with cat B ( $\times 30$ ).

prior to washing, resulted in a significant enhancement of the catalyst activity.

### References

1. Benedikt, G. M.; Goodall, B. L. *Metallocene-Catalyzed Polymers: Materials, Properties, Processing, and Markets*; Plastics Design Library: New York, 1998.
2. Moore, E. P. Jr. *Polypropylene Handbook: Polymerization, Characterization, Properties, Processing, Applications*; New York, 1996.
3. Hagihara, H.; Shiono, T.; Ikeda, T.; Soga, K. *Polymer J* 1997, 29 (3), 224–229.
4. Marques, M. M.; Tait, P. J. T.; Mejlzik, J.; Dias, A. R. *J Polym Sci, Part A: Polym Chem* 1998, 36, 573.
5. Xu, J.; Feng, L.; Yang, S.; Yang, Y.; Kong, X. *Polymer J* 1997, 29 (9), 713–717.
6. Soga, K.; Jin, J.; Kaji, E.; Uozumi, T.; Susuki, Y. *Macromol Symp* 1997, 118, 55.
7. Marques, M. F. V.; Aragao C. Junior, P.; José C. Guimaraes, M.; Coutinho, F. M. B. *Polím Ciê Tecnol* 1998, 3, 26.
8. Xu, J.; Deng, Y.; Feng, L.; Cui, C.; Chen, W. *Polymer J* 1998, 30 (10), 824–827.
9. Ciardelli, F.; Altomare, A.; Conti, G. *Macromol Symp* 1994, 80, 29–44.
10. Soga, K.; Kaminaka, M. *Macromol Chem Phys* 1994, 195, 1369–1379.
11. Kaminaka, M.; Soga, K. *Makromol Chem Rapid Commun* 1991, 12, 367–372.
12. Soga, K.; Kaminaka, M. *Makromol Chem* 1993, 194, 1745–1755.
13. Soga, K.; Kaminaka, M. *Makromol Chem Rapid Commun* 1992, 13, 221–224.
14. Sacchi, M. C.; Tritto, I.; Locatilli, P. *Macromol Rapid Commun* 1995, 16, 581–590.
15. Kamfjord, T.; Wester, T. S.; Rytter, E. *Macromol Rapid Commun* 1998, 19, 505–509.
16. Lee, D.-H.; Yoon, K.-B. *Macromol Rapid Commun* 1997, 18, 427–431.
17. Chien, J. C. W.; He, D. *J Polym Sci, Part A: Polym Chem* 1991, 29, 1963–1967.
18. Lee, D.; Shin, S. *Macromol Symp* 1995, 97, 195–203.
19. Kitagawa, T.; Uozumi, T.; Soga, K.; Takata, T. *Polymer* 1997, 38 (3), 615–620.
20. Kaminsky, W.; Renner, F. *Makromol Chem Rapid Commun* 1993, 14, 239–243.
21. Kaminsky, W. *Macromol Symp* 1995, 97, 79–89.
22. Soga, K.; Kim, H. J.; Shiono, T. *Macromol Chem Phys* 1994, 195, 3347–3360.
23. Lee, D.; Shin, S. *Macromol Symp* 1995, 97, 195–199.
24. Kaminsky, W.; Olabisi, O.; Atiqullah, M. *J Metallocene Sci—Rev Macromol Chem Phys* 519–554, 1997.