

Ethylene Polymerization with Methylaluminoxane/ $(n\text{BuCp})_2\text{ZrCl}_2$ Catalyst Supported on Silica and Silica-Alumina at Different $\text{Al}_{\text{MAO}}/\text{Zr}$ Molar Ratios

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ABSTRACT: Methylaluminoxane (MAO)/ $(n\text{BuCp})_2\text{ZrCl}_2$ metallocene catalytic system was supported on silica and silica-alumina. The Zr loading was varied between 0.2–0.4 wt %, and the MAO amount was calculated to get ($\text{Al}_{\text{MAO}}/\text{Zr}$) molar ratios between 100 and 200, suitable for the industrial ethylene polymerization of supported metallocene catalysts. Catalytic activity was statistically analyzed through the response surface method. Within the ranges studied, it was found that Zr loading had a negative effect on polymerization activity, which increases with the ($\text{Al}_{\text{MAO}}/\text{Zr}$) molar ratio. Catalysts supported on silica-alumina are more active than those supported on silica, needing less MAO to reach similar productivity, which constitutes an important

advantage from an economical and environmental point of view. Supported catalysts were characterized by ICP-AES, SEM-energy-dispersive X-ray spectrometer, and UV-Vis spectroscopy, whereas polyethylenes were characterized by GPC and DSC. Molecular weight and crystallinity are not influenced by Zr loading or ($\text{Al}_{\text{MAO}}/\text{Zr}$) ratio, in the range studied. In general, silica-supported MAO/ $(n\text{BuCp})_2\text{ZrCl}_2$ catalysts give polyethylenes with higher molecular weight and polydispersity but lower crystallinity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 599–606, 2011

Key words: metallocene catalysts; silicas; support; Al/Zr molar ratio, polyethylene

INTRODUCTION

Metallocene catalysts activated by methylaluminoxane (MAO) show high activity in polymerizing several olefins, characterized by a narrow molecular weight distribution (~ 2) and homogeneous chemical composition; in addition, they offer high versatility and flexibility both for the synthesis and the control of the polyolefins structures.^{1–3}

However, despite their plentiful advantages, some technical problems require solution before the extensive use of homogeneous metallocene catalysts in industry as drop in technology in existing plants.^{2,3} One of them is related to the need of large amounts of cocatalyst such as MAO to get the maximum metallocene-catalytic activity. The optimal MAO/metallocene ratio lies between 5000 and 10,000 because of the bimetallic deactivation reactions and the use of MAO as an impurity scavenger, especially in the absence of additional alkyl aluminium compounds.^{3–5}

Although very extensive research has been performed, the exact composition and structure of MAO are still not entirely clear because of the dynamic equilibrium postulated in MAO solutions.⁶

In addition, it is difficult to determine precisely the activation mechanism of metallocenes by MAO; the process must comprise alkylation of the metal atom and subsequent abstraction of one of the methyl or halogen groups from the metallocene, thus generating the catalytically active species, stabilizing the created active centre, and reactivating the inactive metallocene structures.⁷ Despite its unique effectiveness as a cocatalyst compared with other aluminium alkyls and metallocene activators, MAO has some drawbacks such as high cost, because of the expensive AlMe_3 parent compound, the intrinsic danger connected to the use of extremely pyrophoric AlMe_3 , and the very low solubility in aliphatic solvents (it is soluble in aromatic solvents such as toluene) as well as poor storage stability in solution.^{8,9} Therefore, a decrease in the amount of MAO is desired from an economical and environmental point of view.¹⁰

The immobilization of metallocenes on solid supports results in the reduction of MAO/metallocene ratio because the steric hindrance played by the support prevents deactivation by bimolecular processes, a very important deactivation route in the case of homogeneous metallocenes.⁴ In addition, heterogeneous metallocene catalysts give polymer particles replicating support morphology and avoiding reactor fouling problems observed with homogeneous metallocenes.^{11–13} Concerning solid supports, silica is by far the most common support in the

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heterogenization of metallocenes because it has high surface area and porosity, has good mechanical properties, and is stable under reaction and processing conditions.^{11,12} However, the literature also reports the use of others carriers such as Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, AlPO_4 's, Al-MCM-41, and Al-SBA-15, describing the interaction of metallocenes and MAO with aluminium atoms from the support.¹⁴⁻¹⁷ In fact, our previous work¹⁸ reported higher polymerization activity for $\text{MAO}/(\text{nBuCp})_2\text{ZrCl}_2$ supported on silica-alumina instead on conventional silica. This comparison was done at only one ($\text{Al}_{\text{MAO}}/\text{Zr}$) ratio equal to 150 but knowing that for industrially used silica-supported metallocene catalysts the ($\text{Al}_{\text{MAO}}/\text{Zr}$) ratios are in the range 100–300,¹⁹⁻²⁶ it could be interesting to study its influence using both supports and to see if the differences in activity observed between silica and silica-alumina-supported catalysts¹⁸ depend, or not, on the catalysts ($\text{Al}_{\text{MAO}}/\text{Zr}$) ratio. Besides, knowing the higher polymerization activity of silica-alumina-supported $\text{MAO}/(\text{nBuCp})_2\text{ZrCl}_2$ catalysts, it would be possible to reduce the amount of MAO or the ($\text{Al}_{\text{MAO}}/\text{Zr}$) ratio needed to get an activity level similar to the conventional silica-supported metallocenes.

EXPERIMENTAL

Preparation and characterization of supported metallocene catalysts

Heterogeneous metallocene catalysts were prepared by impregnating silica and silica-alumina ($\text{Si}/\text{Al} = 4.8$) supports supplied by Grace-Davison with a solution of MAO (MAO 30 wt % in toluene, Witco, USA) and bis(butylcyclopentadienyl) zirconium dichloride ($(\text{nBuCp})_2\text{ZrCl}_2$, Crompton, USA) in dry toluene (99 wt %, Scharlab, Spain). The amount of MAO and $(\text{nBuCp})_2\text{ZrCl}_2$ was calculated to get supported catalysts with different Al and Zr loadings and the desired ($\text{Al}_{\text{MAO}}/\text{Zr}$) molar ratio. According to our previous results,¹⁸ silica and silica-alumina were firstly calcined at 400°C and 200°C, respectively, for 5 hours under static air conditions; next they were impregnated with the MAO/metallocene solution.

The impregnation procedure was performed at room temperature, in a stirred vessel under inert nitrogen atmosphere during 3 hours. The volume of the impregnating solution was fixed as three-fold the pore volume of the employed support. Finally, a nitrogen stream flowing through the slurry eliminates the toluene solvent drying the supported catalyst without additional washing and filtration steps. Aluminium and zirconium contents of the supported catalysts were determined by ICP-AES on a Varian Vista AX Axial CCD Simultaneous ICP-AES spectrophotometer.

UV-Vis spectroscopic studies of $\text{MAO}/(\text{nBuCp})_2\text{ZrCl}_2$ -supported catalysts were performed

in a Varian Cary 500 spectrophotometer; catalyst samples were sealed, in a glove box, into 1 cm quartz cells with Teflon stoppers. The UV-Vis spectra were scanned (450 nm/min) using an integrating sphere used as diffuse reflectance accessory to enable the measurement in reflectance mode.

Scanning electron micrographs were obtained on a Phillips XL30 ESEM at 15 kV accelerating voltage equipped with an energy-dispersive X-ray spectrometer for chemical analyses. For the cross-section analysis of the catalysts particles, they were embedded in an epoxy resin (low viscosity kit, Spurr, USA) and cured at 70°C for 16 hours; afterward, the samples were cut with a diamond knife in a Leica EM FC6 ultracut microtome at room temperature using standard methods.

Polymerization and polymer characterization

Ethylene polymerizations were performed in a Schlenk tube at 70°C and 1.2 bar of ethylene pressure. Solid catalyst was suspended in 20 mL of heptane and transferred to the Schlenk, having 200 mL of n-heptane as solvent, where tri-isobutylaluminium (TIBA, 30 wt % in heptane, Witco) was added up to reach an ($\text{Al}_{\text{TIBA}}/\text{Zr}$) molar ratio of 800. The amount of TIBA was enough to scavenge impurities but not excessive to substantially inhibit the catalytic activity. After 30 minutes, polymerization reaction was stopped by rapid depressurization of the Schlenk and quenching by addition of acidified (HCl) methanol. The polyethylene obtained was separated by filtration and dried under atmospheric pressure at 70°C. All reactions were performed twice, and the reported activity values are the average between both experiments.

Polymers mean molecular weight and molecular weight distributions were determined by size-exclusion chromatography at 145°C on a Waters 150C Plus instrument, using 1,2,4-trichlorobenzene as mobile phase. The column set consisted of one PL-Gel 10 μm Mixed B (300 \times 7.5 mm) and another Polymer PL-Gel 10 μm 10E6A (300 \times 7.5 mm). Polymer melting point (T_m) and crystallinity were determined using a METTLER TOLEDO DSC822 differential scanning calorimeter, with a heating rate of 10°Cmin⁻¹ from 23°C to 160°C. Two scans were performed but only the results of the second scan are reported because the former is influenced by the mechanical and thermal history of the samples.

RESULTS AND DISCUSSION

Two series of $\text{MAO}/(\text{nBuCp})_2\text{ZrCl}_2$ supported catalysts were prepared by impregnation of silica and silica-alumina carriers with different Al and Zr loadings chosen to get ($\text{Al}_{\text{MAO}}/\text{Zr}$) molar ratios between

TABLE I
Influence of Zr Loading and Al/Zr Molar Ratio on the Polymerization Activity of MAO/(nBuCp)₂ZrCl₂ Catalyst Supported on Silica and Silica-Alumina

Run	Silica			Run	Silica-Alumina		
	Zr (wt %) ^a	Al _{MAO} /Zr ^a	kg PE/mol Zr·h·bar		Zr (wt %) ^a	Al _{MAO} /Zr ^a	kg PE/molZr·h·bar
1	0.20	101.1	235	10	0.21	90	588
2	0.21	151.3	310	11	0.19	140.5	1030
3	0.20	201.7	409	12	0.19	190.3	1300
4	0.30	101.2	200	13	0.31	90.2	559
5	0.30	152.6	320	14	0.29	140.3	604
6	0.29	200.6	433	15	0.30	190.4	775
7	0.41	100.7	95	16	0.40	90.5	279
8	0.40	150.9	190	17	0.40	140.7	406
9	0.40	200.5	253	18	0.40	189.7	510

Polymerization conditions: 70°C, 1.2 bar of ethylene pressure, (Al_{TIBA}/Zr) = 800, time = 30 minutes.

^a Zr loading and Al from MAO to Zr molar ratio determined by ICP-AES.

100 and 200 which are commonly used in silica-supported metallocene catalysts involved in industrial polymerization processes.^{25,26} Their zirconium contents and the (Al_{MAO}/Zr) molar ratio determined by ICP-AES are shown in Table I together with their catalytic activity results in ethylene polymerization.

An important aspect of olefin polymerization using heterogeneous catalysts concerns the distribution of the catalytic species within the carrier solid particles. SEM-energy-dispersive X-ray spectrometer analyses were carried out in cross-sectioned catalyst particles. Although it was not possible to determine Zr by this technique because of the low loadings, the measurements of Al percentage across the silica particles (Fig. 1) can be correlated with the active species (MAO-metallocene, met-MAO-ion pairs) distribution. As it can be observed, the aluminium was well dispersed on the support without significant aluminium concentration gradients inside the solid particles, proving the suitability of the catalyst preparation method.

In the metallocene UV-Vis studies, the bands of most interest are because of the ligand-to-metal charge transfer transitions because they are sensitive to changes in the metal environment such as ligand changes. When MAO reacts with (nBuCp)₂ZrCl₂ abstracting the chloride ions and replacing them with one methyl group, a positive charge decreases the electron density at the Zr atom, which leads to a decrease in the energy of the ligand-to-metal charge transfer transition because electron density is more easily transferred from the electron-rich (nBuCp) ligands to the electron-poor Zr.²⁷⁻²⁹ Figure 2 presents the UV-Vis spectra of MAO/(nBuCp)₂ZrCl₂ catalyst supported on silica and silica-alumina. In general, the broad band placed around 350 nm suggests the presence of monomethylated species like [(nBuCp)₂ZrCH₃]⁺[MAOCl]⁻.^{28,30-32} In addition, the UV-Vis spectra of silica-alumina-supported catalysts show an absorption band at higher wavelenghts

(~ 450 nm) related with the presence of more cationic active species with further ionic pair dissociation. This band only appears in silica-alumina and is more intense at lower Zr loading because at higher Zr percentages, it increases the probability to get zirconocene dimers (i.e., electron deficient bridging complexes of two Zr centers), which compete for Zr atoms reducing the formation of [(nBuCp)₂ZrCH₃]⁺[MAOCl]⁻ active species.

Figure 3 illustrates the ethylene polymerization activity of MAO/(nBuCp)₂ZrCl₂ supported on silica and silica-alumina versus (Al_{MAO}/Zr) molar ratio determined by ICP-AES. As regard to the influence of the support, a comparison between catalysts with the same Zr loading (wt %) shows that higher polymerization activities are reached with the catalytic system supported on silica-alumina. According to the literature, the enhancement in catalytic activity with silica-alumina as support may be related with its acidic character, which better stabilizes the active species in polymerization, as previously described.^{2,14-18} Figure 3 also evidences the possibility to reduce (Al_{MAO}/Zr) ratio with catalysts supported on silica-alumina getting activities very similar to silica supported catalysts; for example, at 0.2 wt % of Zr loading, silica-supported catalyst gives an activity of 409 kg PE/molZr·h·bar at (Al_{MAO}/Zr) = 200, comparable with the activity shown by the silica-alumina catalyst (588 kg PE/molZr·h·bar) but containing less than a half of aluminium from MAO (Al_{MAO}/Zr = 90).

It is also evident that higher activity levels are obtained with catalysts containing lower Zr loading. This inverse relationship between catalyst activity and Zr loading indicates that only a limited proportion of Zr sites are effectively immobilized and activated from zirconocene catalyst. This fact has been previously observed in ethylene polymerization with homogeneous and supported metallocene catalysts^{20,22,33-36} because as explained above in the UV-

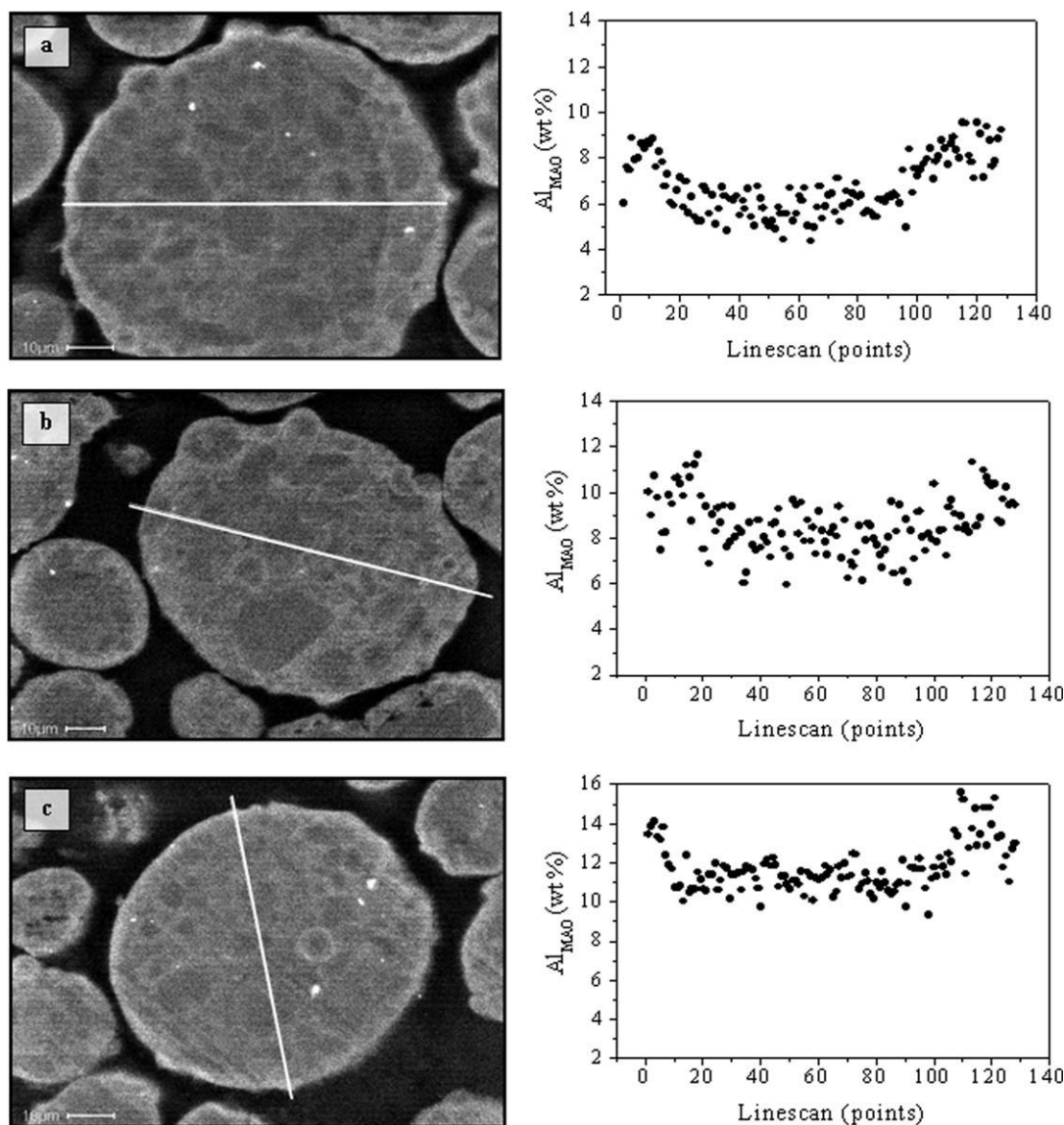


Figure 1 Energy-dispersive X-ray spectrometer analyses of aluminium in the cross-sectioned particles of a silica supported metallocene catalyst with $Al_{MAO}/Zr = 100$ and different Zr loading: (a) 0.2 wt %, (b) 0.3 wt %, and (c) 0.4 wt %.

Vis spectra, at higher Zr loadings, it increases the probability to get zirconocene dimers. These inactive bimetallic species are responsible of the bimolecular deactivation of the metallocene compound.^{37–40} Similarly, at similar Zr amounts, polymerization activity increases as Al_{MAO}/Zr does because MAO forms and stabilizes catalytic active species, preventing the development of inactive zirconocene dimers.^{20,21,33,34} Therefore, at lower Zr loading, there are more spaced catalytic species on the surface, which in turn may guarantee a higher stability against bimolecular deactivation making the mutual approach of Zr centers sterically unfavorable in the bimolecular recombination process.

Zr loadings below 0.2 wt % were not employed in this study because on the contrary very low productivities (gr PE/gr catalyst h) were obtained. More-

over, 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 ethylene polymerization activity was statistically analyzed through the response surface method. The statistical data treatment was performed through the analysis of variance (ANOVA table). The factors or independent variables established were catalysts Zr loading and Al_{MAO}/Zr molar ratio, whereas the response or independent variable measured was the polymerization activity. The statistical data treatment was accomplished by means of the software Statgraphics Plus 5.0.

Table II lists the statistical significance (P values) and the estimated effects of each factor on the

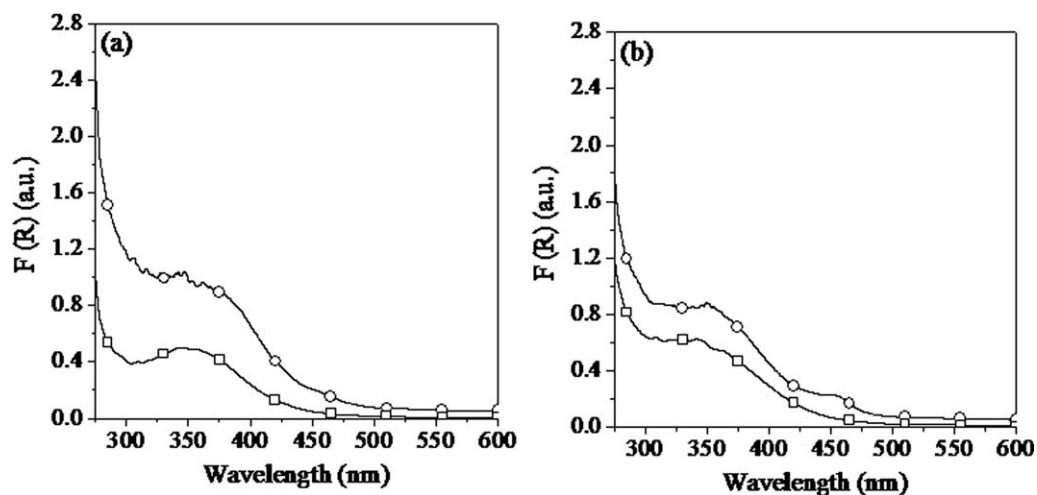


Figure 2 UV-Vis spectra of MAO/(nBuCp)₂ZrCl₂ supported over □-silica ($Al_{MAO}/Zr = 100$) and ○-silica-alumina ($Al_{MAO}/Zr = 90$); (a) Zr : 0.3 wt %; (b) Zr : 0.2 wt %.

polymerization activity over silica and silica-alumina-supported MAO-metallocene catalysts. Only factors with P values < 0.05 are significantly different from zero at the 95% confidence level. Having in mind these figures, both factors (the Al_{MAO}/Zr ratio and the Zr percentage) were significant in the activity of catalysts supported on silica and silica-alumina. However, the interaction between both factors is not significant neither in silica nor in silica-alumina-supported catalysts.

In the ranges studied, the (Al_{MAO}/Zr) ratio and the (Zr) loading have positive and negative effects, respectively. Therefore, the polymerization activity increases by increasing aluminium or decreasing the zirconium loading in the supported catalysts. For silica-supported catalysts, a curvature effect is observed because the Zr^2 factor is also significant.

Knowing that (Al_{MAO}/Zr), (Zr), and (Zr^2) were the relevant factors for silica-supported catalysts, a second order model was considered to fit the polymerization activity results. The parameters of the second order model were determined by multiple regressions, resulting in the next Equation (1):

$$activity \left(\frac{kgPE}{molZr \cdot h \cdot bar} \right) = -377.83 + 3446.67 \cdot Zr + 1.88(Al_{MAO}/Zr) - 6900 \cdot Zr^2 \quad (1)$$

The second-order model can be plotted as a three-dimensional surface representing the response (polymerization activity) as a function of the two factors (Al_{MAO}/Zr) ratio and Zr loading, for the experimental range considered. Figure 4 shows the surface response plot for polymerization activity according to Equation (1). The Al_{MAO}/Zr molar ratio shows stronger influence on the polymerization activity

with a positive effect. More interestingly, Equation (1) indicates that when silica is used as support, catalyst activity exhibits a nonlinear behavior with the zirconium loading; exactly, polymerization activity reaches a maximum (429.25 kg PE/mol Zr-h-bar) at a Zr loading around 0.25 wt %. At higher zirconium contents, a significant decrease in activity is observed, whereas higher Al_{MAO}/Zr ratios always lead to better activity results. The correlation coefficient ($R = 98.03\%$) indicates that the model predicts reasonably the polymerization activity of MAO/(nBuCp)₂ZrCl₂ catalytic system supported on silica within the range studied for both variables.

Similarly, the polymerization activity of MAO/(nBuCp)₂ZrCl₂ supported on silica-alumina was

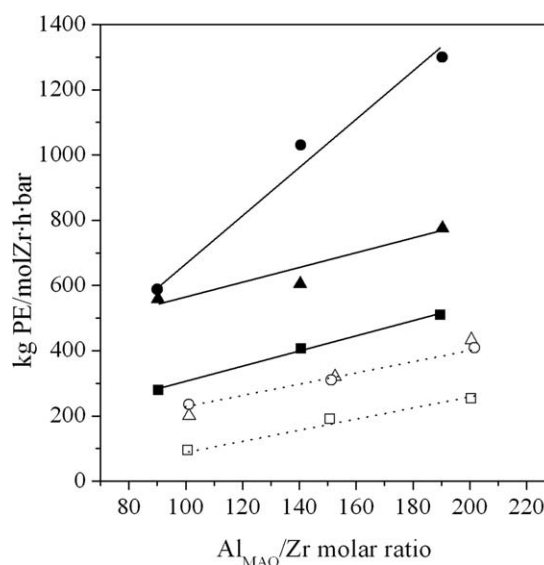


Figure 3 Ethylene polymerization activity with MAO/(nBuCp)₂ZrCl₂ supported over silica (hollow symbols) and silica-alumina (bold symbols) with Zr wt %: ○-●-0.2, △-▲-0.3, and □-■-0.4.

TABLE II
Significance Probability (*P*-Value) and Estimated Effects for Polymerization Activity Obtained with MAO/(*n*BuCp)₂ZrCl₂ Supported on Silica and Silica-Alumina

Factor	<i>P</i> value		Estimated Effects	
	Silica	Silica-Alumina	Silica	Silica-Alumina
Zr	0.0060	0.0053	-138.667	-579.667
Al _{MAO} /Zr	0.0025	0.0169	188.333	383.000
Zr ²	0.0275	0.6291	-138.0	73.6667
Zr(Al _{MAO} /Zr)	0.7628	0.0857	-8.000	-245.500
(Al _{MAO} /Zr) ²	0.8932	0.8812	-5.000	-22.333

fitted to a first-order model, which parameters were also determined by multiple regression, resulting in the next Equation (2) in which response surface plot is shown in Figure 5.

$$\text{activity} \left(\frac{\text{kgPE}}{\text{molZr} \cdot \text{h} \cdot \text{bar}} \right) = 1000.86 - 2898.33 \cdot \text{Zr} + 3.83(\text{Al}_{\text{MAO}}/\text{Zr}) \quad (2)$$

A linear relationship between factors and catalytic activity is observed with a strong negative effect of the zirconium loading in the interval 0.2–0.4 wt %, where polymerization activity decreases continuously. Similarly, as it happens when silica is used as support, the activity is improved by increasing the (Al_{MAO}/Zr) factor. The correlation coefficient (*R* = 88.77 %) showed that the model predicts the polymerization activity somewhat worse than in the case of the silica support within the range of the variables studied.

Polymer properties

Regarding PE properties showed on Table III, no great differences were found to correlate the poly-

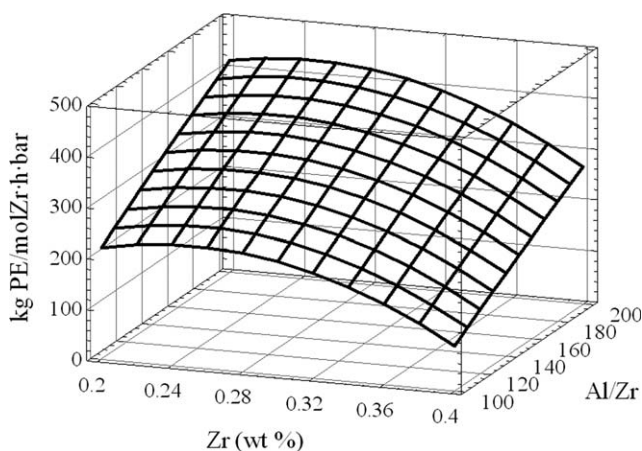


Figure 4 Activity variation surface graph for SiO₂/MAO/(*n*BuCp)₂ZrCl₂ supported catalysts as a function of Zr loading and Al_{MAO}/Zr molar ratio, as Equation (1): *R* = 98.03%.

mer properties with the catalysts Zr loading or Al/Zr molar ratio. Generally speaking, silica-supported catalysts produce polymers with slightly higher molecular weights and polydispersities than polyethylenes obtained with silica-alumina-supported catalysts. So, the chemical composition of the silica-alumina support (Si/Al = 4.8) and the smaller average pore diameter, 18.2 nm versus 28.5 nm of silica,¹⁸ may promote chain transfer reactions,^{41–44} decreasing polyethylene molecular weight with a narrower molecular weight distribution (MWD).

On the other side, melting temperatures determined by differential scanning calorimetry (DSC) are very similar, between 132°C and 134°C, indicating the formation of high density polyethylene with both supports. However, silica-alumina-supported catalysts provide polyethylenes with slightly higher crystallinity values than silica-supported catalysts.

CONCLUSIONS

MAO/(*n*BuCp)₂ZrCl₂-supported catalysts on SiO₂ and SiO₂-Al₂O₃ showed specific polymerization activity levels depending on the zirconium loading; for each level, catalytic activity increases with the Al_{MAO}/Zr ratio because of the stabilization and

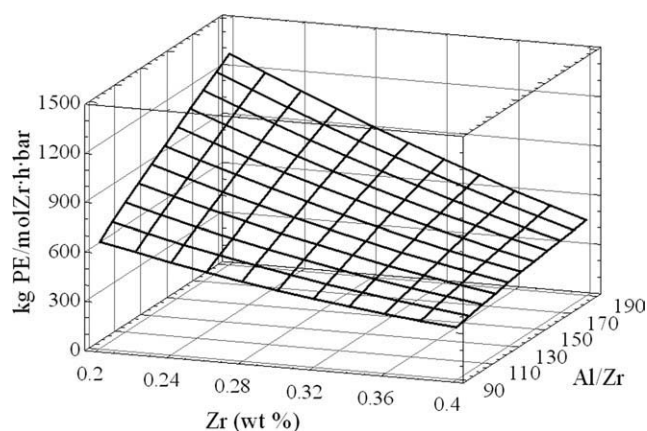


Figure 5 Activity variation surface graph for SiO₂-Al₂O₃/MAO/(*n*BuCp)₂ZrCl₂-supported catalysts as a function of Zr loading and Al_{MAO}/Zr molar ratio, as Equation (2): *R* = 88.77%.

TABLE III
Properties of Polyethylene Synthesized with MAO/(nBuCp)₂ZrCl₂ Catalyst Supported on Silica and Silica-Alumina

Run	Silica			Run	Silica-Alumina		
	M _w	M _w /M _n	Crystallinity (%)		M _w	M _w /M _n	Crystallinity (%)
1	206,540	3.62	57	10	161,407	2.55	58
2	183,465	3.56	59	11	164,267	2.69	60
3	172,404	3.63	58	12	165,687	2.81	60
4	169,858	3.61	59	13	156,079	2.79	60
5	146,442	3.63	57	14	147,665	3.09	62
6	147,216	3.64	60	15	143,797	3.07	62
7	147,298	3.10	58	16	175,124	2.71	59
8	147,981	3.24	58	17	159,566	2.89	61
9	150,267	3.66	54	18	151,251	2.95	62

reactivation role of MAO as cocatalyst. Lower polymerization activities were reached at higher Zr loadings probably because of the dimerization of the metallocene complexes in the MAO/metallocene solution, which led to an inefficient production of active sites during the supporting process.

UV-Vis spectra of supported catalysts showed that, at equivalent Zr (wt %) and Al/Zr molar ratio, silica-alumina-supported catalysts present more active species (mono or dimethylated zirconocene molecules) with a further ionic character than those found in silica-supported catalysts.

The catalyst activity was statistically analyzed through response surface methods. In the ranges studied (0.2–0.4 wt % of Zr and 100–200 of Al_{MAO}/Zr molar ratio), it was found that catalyst Zr loading had a negative effect on polymerization activity, whereas higher activities are achieved by increasing the (Al_{MAO}/Zr) factor. Catalysts supported on silica-alumina gave high polymerization activities with lower (Al_{MAO}/Zr) molar ratios, which constitute an important advantage from an economical and environmental point of view.

Polyethylenes obtained with silica-alumina-supported catalysts present slightly lower molecular weight and polydispersity and higher crystallinity than polyethylene obtained with silica as a carrier. In this sense, aluminium atoms from the support may favor chain transfer reactions and the stabilization of zirconocene active species. Besides, catalysts supported on silica-alumina produce polyethylenes very similar in their properties, which are almost independent of the (Al_{MAO}/Zr) molar ratio used in the range between 90 and 190.

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