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Heterogeneous Polymerization of Ethylene and 1-Hexene with $Me_3SiCp_2ZrH_3AlH_2/SiO_2$ Activated with MAO

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Summary: The aluminohydride of zirconocene $Me_3SiCp_2ZrH_3AlH_2$ was supported on pre-treated SiO_2, and its catalytic activity for ethylene polymerization and ethylene-1-hexene copolymerization was evaluated in order to compare with the corresponding activity of the complex in solution. As expected for systems based on metallocenes, the aluminohydride of zirconocene complex showed higher activity in solution than in suspension, however its thermal and kinetic stability was significantly increased. The effect of the co-catalyst concentration (MAO) on the activity and the molecular weight of the polymers are also reported in this study, finding that in heterogeneous phase low concentrations of MAO were used to activate the pre-catalyst. The MW of the polymers and copolymers synthesized with the supported $Me_3SiCp_2ZrH_3AlH_2/SiO_2$ could be controlled by adding molecular hydrogen (H_2) as chain transfer agent in the polymerization and copolymerization reactions.

Keywords: aluminohydride of zirconocene; ethylene and 1-hexene copolymerization; H_2 effect; heterogeneous polymerization

Introduction

Advances in olefin polymerization using single site catalysts (SSC), based on metallocenes, have produced many grades of polyolefins with precise control of their microstructures, molecular weights (MW) and molecular weight distributions (MWD).[1]

In order to be used in industrial slurry or gas phase processes, metallocene compounds have been heterogenized on different kinds of inorganic supports, by means of several methods reported in the literature.[2] The most applied method for supporting metallocenes, involves the use of silica, previously modified with MAO (SiO_2/MAO) according to the route summarized by Ribeiro et al.[2a]

In previous work, we reported the use of a metallocene system based on zirconocene aluminohydride complexes, activated with the Lewis acids $B(C_6F_5)_3$ and MAO, for ethylene polymerization in homogeneous phase. The catalytic system showed very high activities, 40–50% superior to the traditional activation method involving the corresponding zirconocene dichlorides and MAO.[3]

Zirconocene aluminohydride complexes have been studied in detail since 1990 by several research groups.[4,5] They reported a dynamic association of zirconocene dihydrides and alane (AlH_3) in solution, which in the case of $Me_3SiCp_2ZrH_3AlH_2$, led to the formation of three different aggregates that co-crystallized in the unit cell.[4b]

These complexities of the aluminohydrides of zirconocenes were considered in

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further applications as pre-catalysts in homogeneous polymerization reactions,[3] as well as in heterogeneous phase, by supporting the zirconocene aluminohydrides on MAO-modified silica.[6]

The aim of this work was to evaluate the $Me_3SiCp_2ZrH_3AlH_2$, supported on MAO-modified silica (SiO_2/MAO), in the polymerization and copolymerization of ethylene and ethylene-1-hexene in slurry phase, and compare with results obtained from experiments carried out in homogeneous phase. The control of the molecular weight (MW) in the polymers was achieved through the addition of molecular hydrogen (H_2) as chain transfer agent. The effect of the H_2 addition and the co-catalyst ratio on the activity is also reported in this work.

Experimental Part

Synthesis of $Me_3SiCp_2ZrH_3AlH_2$

The $Me_3SiCp_2ZrH_3AlH_2$ was synthesized by the modified method reported by Stephan and co-workers.[4b] A solution of $Me_3SiCp_2ZrCl_2$ (1.99 g, 4.55 10^{-3} mol) in diethyl ether (50 mL) was stirred at 0 °C and 2.2 equiv of $LiAlH_4$ (0.01 mol) in diethyl ether (10 mL) was added dropwise during 10 min. The formation of a fine white powder was observed when the mixture was allowed to warm to room temperature (30 min) and the solution was filtered. The diethyl ether was evaporated to provide the corresponding zirconocene aluminohydride in quantitative crude yield, which was dissolved in toluene (30 mL) prior to further use.

Supporting of the Pre-Catalyst $Me_3SiCp_2ZrH_3AlH_2$

The supported pre-catalyst was prepared according to a general method reported for metallocene dichloride complexes.[2] A solution of MAO in toluene (15.0 mL of a 10 wt% prepared from previously vacuum dried, solid MAO) was added to a suspension of SiO_2 (1 g SiO_2/20 mL of toluene), previously dehydrated for 6 h at 800 °C. The addition of the MAO solution was carried out at 0 °C, and then the mixture was allowed to warm to room temperature for 1 h. Then the suspension was heated at 50 °C for 2 h. The slurry was filtered and washed twice with toluene to obtain the MAO-modified silica (SiO_2/MAO). The 13 wt.-% of aluminium content was determined on the SiO_2 by atomic absorption (AA) analysis and was 13.0 wt% Al.

A toluene solution of $Me_3SiCp_2ZrH_3AlH_2$ (4.5 10^{-3} mol/30 mL toluene) was added dropwise to 1 g of SiO_2/MAO suspended in 30 mL of toluene. The addition was carried out at 0 °C and then the mixture was stirred for 12 h at room temperature. The slurry was filtered, washed twice with toluene and dried in vacuum for 6 h. The content of Zr (2.4 wt. %) was determined by AA analysis, and the supported pre-catalyst $Me_3SiCp_2ZrH_3AlH_2$/SiO_2/MAO was stored in a glove box prior to use.

Polymerization Reactions

The aluminohydride complex was activated with the corresponding amount of a 10 wt. % solution of MAO in toluene at room temperature for about 5 min, and in all the cases the solutions or suspensions were transferred by syringe into the reactor. Polymerizations were carried out in a 600 mL Parr reactor equipped with mass flow meter and temperature control. Before each reaction, the reactor was heated up for 1 hour to 90 °C with $AlMe_3$/toluene to remove all moisture traces.

Polymerization conditions for all the runs were: ethylene pressure of 42 psig, or 42 psig of a mixture of ethylene/hydrogen (C_2/H_2), 200 mL of isooctane, polymerization temperature of 50 or 70 °C. The monomer flow rate was continually monitored through the mass flow meter and the polymerizations were carried out for 1 h.

The polymerization was stopped by rapid de-pressurization of the reactor and quenching with acidified methanol (10 wt % HCl). Then, the polymers were washed several times with methanol, filtered and dried in a vacuum oven during 4 hours.

Results and Discussion

Table 1 shows the results of ethylene homopolymerization experiments using the supported pre-catalyst, Me_3SiCp_2Zr-H_3AlH_2/SiO_2/MAO, activated at different Al/Zr ratios, comparing with some experiments carried out in homogeneous phase in a previous work.[3]

As expected for metallocene systems, homogeneous polymerizations showed higher catalytic activities than those observed for slurry reactions, however, a very high concentration of co-catalyst (MAO) was used to activate the catalytic system in solution (Entries 1*–2* and 3–6). As for heterogeneous reactions, the amount of MAO contained in the support (modified silica) was not considered in the Al/Zr ratio reported in Table 1 data, since these correspond to 0.1 to 0.2×10^{-3} mol according to the amount of supported catalyst used in most of the polymerization reactions (0.03 to 0.06 g).

Molecular weights (MW) of the polymers obtained with the supported catalyst activated at different Al/Zr ratios are considerably higher than those obtained for the polymerizations in solution. The above can be related to the well known aluminum chain transfer reactions at high concentrations of co-catalyst in solution, however there are several reports comparing heterogeneous and homogeneous systems, even at the same Al/Zr ratios in their activations, where the conclusion is that the polymers obtained in homogeneous phase have lower molecular weights than those obtained in heterogeneous phase. This fact was attributed to the blocking of the active sites in the immobilized catalysts reducing its activity. Also, the deactivation step through the β-elimination transfer reaction of hydrogen in the metallocene center could be prevented producing larger growth of the polymer chains in the heterogeneous phase polymerizations.[7]

From these results, subsequent experiments were carried out at low concentrations of total MAO (Al/Zr = 500–200), and different amounts of hydrogen (H_2) were employed in the polymerization reactions in order to control the MW of polyethylenes formed.

As can be noticed in Table 2, polymerizations carried out in the presence of H_2 exhibited higher activities at these low Al/Zr ratios. At Al/Zr = 5000, and 4.1 psig of H_2 the activity increased 25% compared to the reaction carried out without H_2 at the same polymerization conditions (Entries 1 and 3).

At lower concentrations of H_2 and similar Al/Zr ratios, an increase of the activity around 80% (entry 2 compared to 4–9) was observed, remaining low concentrations of co-catalyst.

Figure 1 shows the effect of the co-catalyst concentration on the activity and the MW, maintaining a constant pressure of H_2 (4.1 psig), where the height of the bars correspond to the activity and the symbol (·) to the Mw of the polymers.

A slight variation of the activity (±15%) was observed when increasing the Al/Zr ratio, at constant concentration of H_2

Table 1.
Ethylene homopolymerization using the $SiMe_3$-$CpMe_3SiCp_2ZrH_3AlH_2$ in homogeneous and heterogeneous phase.

Entry	Al/Zr	Act	Mn	M_W	M_W/Mn
		Kg PE/mol h	g/mol	g/mol	
1*	40000[a)]	58100	25400	81400	3.2
2*	40000[b)]	56300	15600	51500	3.3
3	5000	497	63700	175000	2.7
4	400	544	310080	84600	2.7
5	400	400	49500	98300	2.0
6	300	212	46100	150000	3.2

Isooctane (200 mL), T = 70 °C, P = 42 psig, [cat] = $1–2 \times 10^{-5}$ M, t = 1 h, 500 rpm. *Homogeneous phase (isooctane), a)T = 70 °C, b)T = 50 °C.

Table 2.
Ethylene homopolymerization using the $SiMe_3$-$CpMe_3SiCp_2ZrH_3AlH_2$ in heterogeneous phase. Effect of the H_2 on MW.

Entry	Al/Zr	C_2 (H_2)	Act	Mn	M_W	M_W/Mn
			Kg PE/mol h	g/mol	g/mol	
1	5000	C_2	496	63700	175000	2.7
2	400	C_2	400	49500	98300	2.0
3	5000	C_2 (4.1psig H_2)	629	691	1930	2.7
4	400	C_2 (4.1psig H_2)	726	1010	2600	2.5
5	300	C_2 (4.1psig H_2)	624	678	1670	2.4
6	300	C_2 (2.5psig H_2)	2600	6040	16600	2.7
7	500	C_2 (1.6psig H_2)	755	32400	62400	1.9
8	400	C_2 (0.8psig H_2)	1310			
9	200	C_2 (0.8psig H_2)	2150	13100	34100	2.6

Isooctane (200 mL), $T = 70\,^\circ C$, $P = 42$ psig, $[cat] = 1\text{–}2 \times 10^{-5}$ M, $t = 1$ h, 500 rpm.

(4.1 psig). The above suggests that this variation in activity could be within the experimental error and there is no a significant influence of the co-catalyst concentration on the activity at constant H_2 pressure.

The positive effect of H_2 addition on the catalytic activity has also been reported for different Ziegler-Natta and metallocene catalysts in slurry polymerizations.[8–10] Some explanations have attributed this effect to the possible increase of the propagation rate constant related to the reactivation for dormant sites with hydrogen, or to the increase of the rate of chain transfer reactions compared to polymerizations without hydrogen. [7a]

Figure 2 shows the effect of different hydrogen concentrations on the activity of the catalyst and MW of the polyolefins produced at different Al/Zr ratios. The height of the bars correspond to the activity and the symbol (·) to the Mw of the polymers obtained at the corresponding hydrogen partial pressure.

As expected, the MW of homopolymers decreased with H_2 addition, and the polydispersity showed typical values of polymers obtained with metallocene systems. Narrow polydispersities were obtained for slurry polymerizations in the presence of H_2, comparable to the polymerizations carried out without H_2 addition (entries 1–2 Table 2).

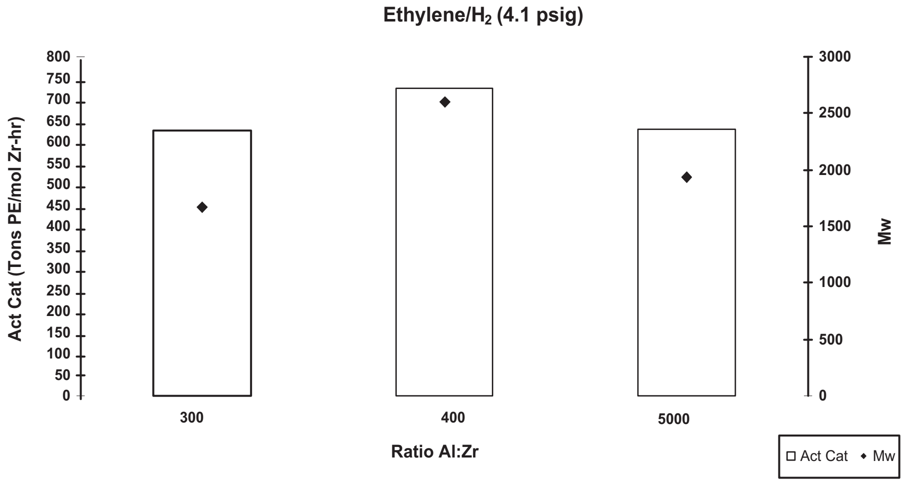

Figure 1.
Effect of the Al/Zr ratio on the activity and MW of the polyethylene at 4.1 psig of H_2, obtained with $Me_3SiCp_2ZrH_3AlH_2/SiO_2/MAO$.

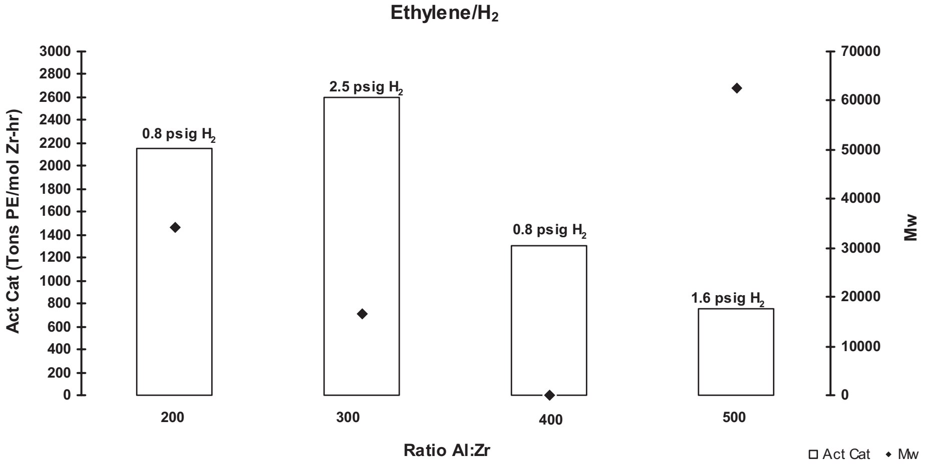

Figure 2.
Effect of H_2 pressure on the activity of the $Me_3SiCp_2ZrH_3AlH_2/SiO_2/MAO$ and MW of the polyethylenes produced using different Al/Zr ratios.

The polymerizations carried out using 0.8 psig of H_2 and Al/Zr = 200 showed good catalytic activity (2150 Kg PE/mol h), and high MW (Mw = 34,100 g/mol) in heterogeneous phase, and this condition was selected to carry out preliminary copolymerization reactions of ethylene and 1-hexene.

Table 3 shows the results of the copolymerization reactions of ethylene and 1-hexene at 10 and 20 wt. % of co-monomer, carried out at 0.8 psig of H_2 concentration, Al/Zr = 300, using isooctane as solvent at 70 °C, and a total pressure of 42 psig of a mixture of ethylene/H_2. The copolymerization reactions were carried out during 1 h, and the results are compared in Table 3 with the features of the corresponding homopolymer obtained under similar conditions (Entry 9, Table 2).

As it can be seen in Table 3, catalytic activity of the supported catalyst and the MW of the copolymers tend to decrease at higher concentrations of comonomer. Although the experiment carried out at 20 wt-% of 1-hexene showed the highest comonomer content (determined by ^{13}C NMR spectroscopy), the activity of the system was diminished 60%, compared to the activity of the homopolymerization reaction, and the copolymer produced exhibited lower MW.

Figure 3 shows the differential scanning calorimetry (DSC) thermograms of the polyethylene and poly(ethylene-1-hexene) copolymers produced with the supported catalyst, where one can observe a decrease in both crystallization (T_c) and melting (T_m) temperatures, for the copolymers.

The copolymer curves are broader than that of the homopolymer (Figure 3), which indicates a higher disorder in the crystalline structure, due to the presence of branching

Table 3.
Copolymerizations of Ethylene and 1-Hexene in Heterogeneous phase with $Me_3SiCp_2ZrH_3AlH_2/SiO_2/MAO$.

Hexene (wt. %)	Act	Mn	M_W	M_W/Mn	Tm (°C)	ΔH°m	*wt %
	Kg PE/mol h	g/mol	g/mol			J/g	Hexene
0	2150	13100	34100	2.6	134	222.5	0
10	2060	10300	27300	2.6	127	175.6	0.4
20	881	6660	13400	2.0	115	115.6	2.0

Isooctane (200 mL), T = 70 °C, P = 42 psig (C_2), 0.8 psig H_2 [cat] = $1–2 \times 10^{-5}$ M.
Al/Zr = 200, t = 1 h, 500 rpm* ^{13}C NMR spectroscopy.

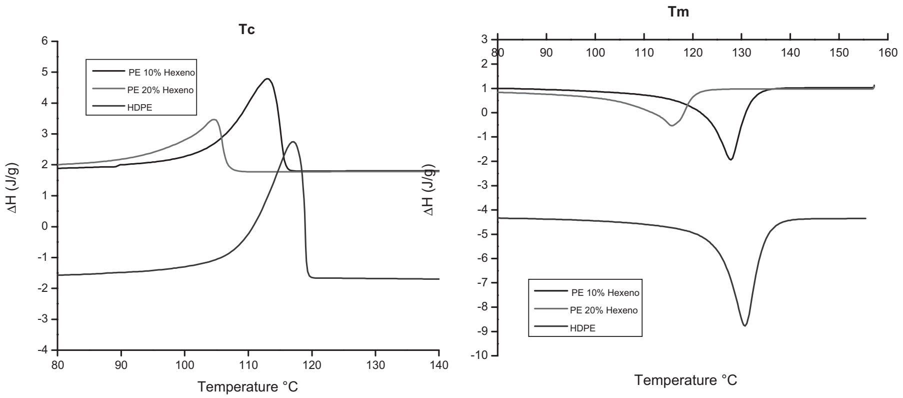

Figure 3.

DSC (Tc) and (Tm) of polyethylene and poly(ethylene-1-hexene) copolymers at 10 and 20 wt.-% of 1-hexene obtained with the supported $Me_3SiCp_2ZrH_3AlH_2/SiO_2/MAO$.

from comonomer incorporation. The heat of fusion (ΔH^om) reported in Table 3 also tends to decrease with the increase of the comonomer addition, which supports the lower crystallinity of the copolymers compared to the homopolymer synthesized under similar conditions.

The results in all the cases (homopolymers and copolymers) showed the formation of particles of low molar mass that could be related to some level of dissolved metallocene (leaching) from the support under the polymerization conditions utilized in these experiments, as reported for supported metallocenes.[11,12] In other experiments we probed the leaching of the derivative aluminohydride of zirconocene ($nBuCp_2ZrH_3AlH_2/SiO_2/MAO$) by filtering the supported catalyst after its activation with soluble MAO containing TMA. The activity of the filtered system decreased only 35% compared to the unfiltered experiment, which suggests that a high percentage of polymer could have been formed in homogeneous phase. The same situation could occur for the supported derivative $SiMe_3Cp_2ZrH_3AlH_2$ studied in the present work; however, we would have to probe the leaching phenomenon through similar polymerization experiments.

Conclusions

The supported $Me_3SiCp_2ZrH_3AlH_2/SiO_2/MAO$ system evaluated in the polymerization of ethylene in slurry phase showed high catalytic activity, and high molecular weights (MW) using different ratios of co-catalyst (MAO). The activities were lower than those obtained in homogeneous phase; however, a considerable reduction in the co-catalyst (MAO) addition was achieved, and the MW of the polyethylenes could be controlled by H_2 addition. Ethylene homopolymerization at 0.8 psig of H_2 and low co-catalyst ratio ($Al/Zr = 200$), showed high activity and MW, and these conditions were used to carry out preliminary copolymerization experiments of ethylene and 1-hexene. The supported $Me_3SiCp_2ZrH_3AlH_2/SiO_2/MAO$ exhibited lower catalytic activity using 1-hexene as comonomer at low Al/Zr ratios; however, from these preliminary results, the potential of the supported aluminohydride zirconocene complexes is clearly demonstrated.

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