

## Homogeneous and Heterogeneous Ethylene Polymerization with the Aluminohydride of Zirconocene $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2$ Activated with MAO

Rebeca González<sup>1</sup>, Elsa Elena Morales<sup>1</sup>, Maricela García<sup>1</sup>, Javier Revilla<sup>2</sup>, Rogelio Charles<sup>2</sup>, S. Collins<sup>3</sup>, and Odilia Pérez<sup>1\*</sup>

<sup>1</sup>*Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna 140 Saltillo, Coah. México C.P. 25253 e-mail: [odilia@ciqa.mx](mailto:odilia@ciqa.mx)*

<sup>2</sup>*Centro de Investigación y Desarrollo Tecnológico, Ave. de los Sauces No. 87, Parque Industrial Lerma, Edo. de México, C.P. 52000 e-mail: [javier.revilla@desc.com.mx](mailto:javier.revilla@desc.com.mx)*

<sup>3</sup>*Department of Polymer Science, University of Akron 170 University Circle, Akron OH 44325-390.*

### Summary

Recently we reported that aluminohydride zirconocene complexes (generically  $\text{Cp}_2\text{ZrH}_3\text{AlH}_2$ ) could be activated using methylaluminoxane (MAO) for homogeneous ethylene polymerization, where polymerization activity was superior (40-50%) to the traditional activation method involving the corresponding zirconocene dichlorides and MAO.<sup>1</sup> In this work, the  $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2$  was supported on pre-treated  $\text{SiO}_2$ , and its catalytic activity for ethylene polymerization could be evaluated in heterogeneous phase, in order to compare to the activity of the complex in solution using MAO as co-catalyst. As expected for systems based on metallocenes, the  $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2$  showed higher activity in solution than in heterogeneous phase, however, the thermal and kinetic stability of the supported complex was significantly increased. Reduced quantities of MAO were used to activate the supported aluminohydride, obtaining PE of high Mw. The control of the Mw using molecular hydrogen ( $\text{H}_2$ ) as chain transfer agent was also studied for the supported zirconocene aluminohydride.

### Introduction

Advancements in olefin catalysis using single site catalysts (SSC) have produced many grades of polyolefins with precise control of their microstructures, molecular weights (MW) and molecular weight distributions (MWD).<sup>1</sup>

In order to be used in industrial slurry or gas phase processes, metallocene catalysts have been heterogenized in different kind of inorganic supports, by means of several methods reported in the literature.<sup>2</sup> The most applied method for supporting metallocenes, involves the use of modified silica previously treated with MAO ( $\text{SiO}_2/\text{MAO}$ ) according to the route reported by Ribeiro et. al.<sup>2a</sup>

Recently, we reported the use of a metallocene system, based in zirconocene aluminohydride complexes, activated with Lewis acids such as  $\text{B}(\text{C}_6\text{F}_5)_3$  as well as with MAO in homogeneous phase, for ethylene polymerization.<sup>3</sup> The structure and features of this kind of complexes, like thermal stability, and different state of aggregation was studied since 1990 for several research groups, and this was taken into account for further studies in polymeric catalysis.<sup>4</sup>

The aim of this work was to evaluate the heterogenized  $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2$ , supported on modified silica ( $\text{SiO}_2/\text{MAO}$ ), in the polymerization of ethylene in slurry phase, comparing these results with that obtained in homogeneous phase. The  $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2$  was supported according to the method used for metallocene complexes.

The control of the molecular weight (MW) through the addition of molecular hydrogen ( $H_2$ ) as chain transfer agent was considered in these studies, as well as some preliminary copolymerizations of ethylene and 1-hexene.

### Experimental Part

#### *Synthesis of $SiMe_3-Cp_2ZrH_3AlH_2$*

The  $SiMe_3-Cp_2ZrH_3AlH_2$  was synthesized by the modified method reported by Stephan and co-workers.<sup>[7]</sup> A solution of  $nBu-Cp_2ZrCl_2$  (1.99 g,  $4.55 \cdot 10^{-3}$  mol) in diethyl ether (50 mL) was stirred at  $0^\circ C$  and 2.2 equiv of  $LiAlH_4$  (0.01 mol) in diethyl ether was dropped 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 yield, which was dissolved in toluene (30 mL).

#### *Supporting of the pre-catalyst $SiMe_3-Cp_2ZrH_3AlH_2$*

The supported pre-catalyst was prepared according to the method reported for metallocene complexes.<sup>4b</sup> 15 mL of a 10 wt.-% solution of PMAO (without TMA) in toluene was added to a suspension of  $SiO_2$  (1 g  $SiO_2$ /20 mL of toluene) previously dehydrated for 6 h at  $800^\circ C$ . The addition of the PMAO solution was carried out at  $0^\circ C$ , and then the mixture was allowed to warm to room temperature for 1 h. Then suspension was heated at  $50^\circ C$  for 2 h. The slurry was filtered and washed twice with toluene to obtain the modified silica ( $SiO_2$ /MAO).

A toluene solution of  $SiMe_3-Cp_2ZrH_3AlH_2$  ( $3.2 \cdot 10^{-3}$  mol/30 mL toluene) was dropped to 1 g of modified silica ( $SiO_2$ /MAO) suspended in 30 mL of toluene. The addition was carried out at  $0^\circ C$  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 (1.59 wt.-%) was determined by atomic absorption (AA), and the supported pre-catalyst  $nBu-Cp_2ZrH_3AlH_2/SiO_2/MAO$  was stored in a glove box.

#### *Polymerization Reactions*

The aluminohydride complex was activated with MAO in toluene, and in all the cases the solutions were transferred by syringe to 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  $90^\circ C$  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 the mixture ethylene/hydrogen ( $C_2/H_2$ ), 200 mL of isooctane, polymerization temperature at 50 or

70°C. The monomer flow rate was continually monitored through the mass flow meter and polymerizations were carried out for 1 h.

The polymerization was stopped by rapid depressurization of the reactor and quenching with acidified methanol (10 wt % HCl) for  $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2/\text{SiO}_2/\text{MAO}$ . Then the polymers were washed several times with methanol, filtered and dried in a vacuum oven during 4 hours.

## Results and Discussions

Table 1 shows the results of the ethylene polymerization experiments using the supported catalyst  $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2/\text{SiO}_2/\text{MAO}$ , evaluated at different Al/Zr ratios with several contents of molecular hydrogen ( $\text{H}_2$ ) as chain transfer agent.

As expected for activations carried out in homogeneous phase, the system showed higher activity than the heterogeneous polymerizations, although higher concentration of co-catalyst, was utilized to activate the system (compare experiments 1-3 and 11-12). As is noticed in Table 1, polymerizations carried out in the presence of  $\text{H}_2$  exhibited higher activities at lower Al/Zr ratios (Exps. 4 -10). The polymerizations carried out using between 0.8 and 4.1 psig of  $\text{H}_2$  showed the highest activities in slurry phase. As expected, the MW decreased in the presence of  $\text{H}_2$ , and the polydispersity showed characteristic values of polymers obtained with metallocenes.

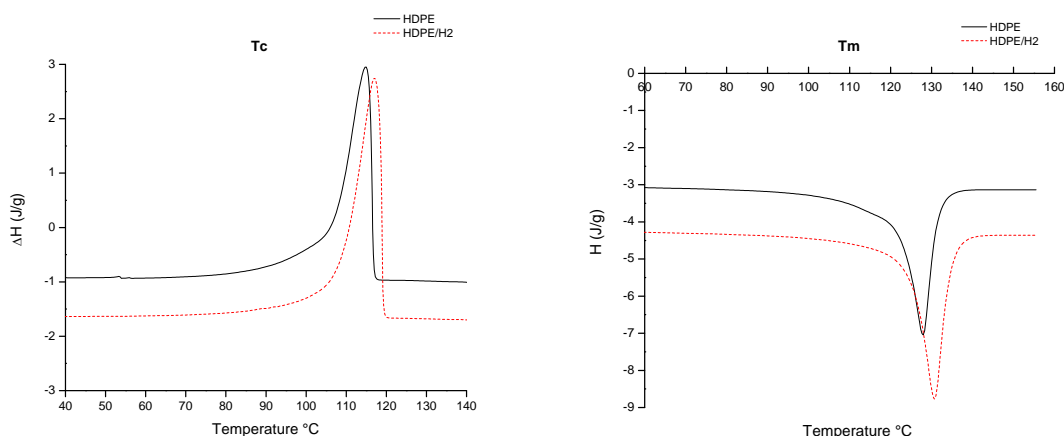
Figure 1 shows the differential scanning calorimetry (DSC) thermograms of the polyethylene produced with the supported catalyst with and without  $\text{H}_2$  addition, where can be observed the effect of the MW, in the crystallization ( $T_c$ ) and melting ( $T_m$ ) temperatures.

**Table 1. Polymerization of ethylene using the  $\text{SiMe}_3\text{-Cp}_2\text{ZrH}_3\text{AlH}_2$  in homogeneous and heterogeneous phase**

Exp	Al/Zr	$\text{C}_2$ ( $\text{H}_2$ )	Act Kg PE/mol h	Mn g/mol	Mw g/mol	Mw/Mn
1	5000	$\text{C}_2$	496.46	63709	174711	2.7
2	400	$\text{C}_2$	543.90	31008	84590	2.7
3	300	$\text{C}_2$	212.26	46080	149883	3.2
4	5000	$\text{C}_2$ (4.1psig $\text{H}_2$ )	629.35	691	1934	2.7
5	400	$\text{C}_2$ (4.1psig $\text{H}_2$ )	725.86	1012	2596	2.5
6	300	$\text{C}_2$ (4.1psig $\text{H}_2$ )	624.31	678	1672	2.4
7	300	$\text{C}_2$ (2.5psig $\text{H}_2$ )	2604.68	6039	16625	2.7
8	500	$\text{C}_2$ (1.6psig $\text{H}_2$ )	755.18	32409	62398	1.9
9	400	$\text{C}_2$ (0.8psig $\text{H}_2$ )	1309.58			
10	200	$\text{C}_2$ (0.8psig $\text{H}_2$ )	2152.38	13080	34132	2.6
11*	40000 <sup>a</sup>	$\text{C}_2$	58100	25437	81400	3.2

12 <sup>*</sup>	40000 <sup>b</sup>	C <sub>2</sub>	56300	15606	51500	3.3
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Isooctane (200 mL), T = 70 °C, P = 42 psig, [cat] = 1-2 X 10<sup>-5</sup> mol/L, t = 1 h, 500 rpm <sup>a</sup> Homogeneous phase (isooctane), <sup>a</sup> T = 70°C, <sup>b</sup> T = 50°C



**Figure 1.** DSC (T<sub>c</sub>) and (T<sub>m</sub>) of the polyethylenes obtained of the exp 2 — (M<sub>w</sub> = 84,590 g/mol) and exp 10 ---- (M<sub>w</sub> = 34,132 g/mol)

The light shift of the curves (~5°C), for the polymers is attributed to the highest facility of crystallization of the polyethylene of lower MW.

## Conclusions

The supported SiMe<sub>3</sub>-Cp<sub>2</sub>ZrH<sub>3</sub>AlH<sub>2</sub>/SiO<sub>2</sub>/MAO system evaluated in the polymerization of ethylene in slurry phase showed high activities, and high molecular weights (MW) using different ratios of co-catalyst (MAO). The activities were lower than that 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<sub>2</sub> addition.

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