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Novel supported catalysts for ethylene polymerization based on aluminohydride-zirconocene complexes

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ABSTRACT

Ethylene polymerization using catalysts derived from activation of zirconocene aluminohydride complexes, supported on silica, pretreated with methylaluminoxane (MAO), is described. The novel catalyst compositions were compared to those using conventional zirconocene dichloride complexes and characterized by SEM/EDX and DRIFT spectroscopy. Supported catalysts were prepared which featured various surface Al:Zr ratios. When using excess MAO as both activator and scavenger, the catalysts containing the most Zr per g of support gave rise to the most active formulations; the high activities in the presence of excess MAO are due, in part, to catalyst leaching prior to and/or during polymerization. When triisobutylaluminum (TIBAL) was used as scavenger, the supported catalysts that featured a higher surface Al:Zr ratio had higher activity than those prepared at the lower Al:Zr ratios. The activity of the aluminohydride complexes was significantly higher than that of the corresponding dichloride complexes, when activated by MAO while the in the presence of TIBAL, there was little difference in performance between the two catalyst precursors.

1. Introduction

Supported catalysts based on metallocene complexes of the group 4 elements are in commercial use for the production of poly(olefins). While a wide variety of approaches to the supporting of metallocene complexes have been investigated [1], by far the most common approach involves reaction of a metallocene dichloride with silica that has been pre-treated with methylaluminoxane (MAO) or with an alkylaluminum compound that can generate MAO on the support [2].

These chemically treated supports chemisorb significant quantities of metallocene dichloride complexes, though not all of the metal on the support is alkylated or activated for olefin polymerization. In particular, the patent literature emphasizes the use of supported catalysts where the surface Al:Zr ratio is between 100:1 and 10:1 as giving rise to the most active formulations based on the amount of Zr present [2].

In contrast, less work has been focused on the use of metallocene dialkyls or related compounds as supported catalyst precursors, despite the generally higher chemoselectivity such complexes exhibit on reaction with hydroxylated supports (i.e. exclusive reaction at the Zr-R bond [3]) and the ease with which such supported catalysts can be activated using e.g. reduced quantities of MAO [3g]. On the other hand, using MAO- or alkylaluminum-treated silica supports, there is no compelling advantage to using such precursors [4].

Two years ago we reported that zirconocene aluminohydride complexes (generically $Cp_2ZrH_3AlH_2$ [5]) could serve as precursors to single-site ethylene polymerization catalysts using either MAO or $B(C_6F_5)_3$ as activators [6]. On activation with MAO in solution, these complexes exhibited superior activity to the corresponding dichloride complexes (ca. 40–50% higher activity) while furnishing polymer with higher molecular weights (by up to a factor of two). Based on multi-nuclear NMR spectroscopic studies, ionization of these polynuclear complexes with $B(C_6F_5)_3$ furnished polynuclear catalysts at low T in solution (e.g. Eq. (1)).

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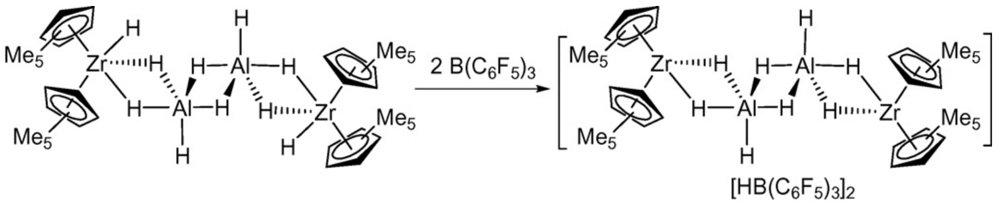

(1)

It is known that catalyst nuclearity can significantly influence both activity and MW in constrained geometry catalysts or phenoxyimine complexes that feature dinuclear catalysts or catalyst precursors [7]. It is thus tempting to attribute the differences seen to the differing nuclearity of the catalyst precursors (or catalysts) in the case of the aluminohydride complexes.

In view of these attractive features we have investigated the preparation of supported versions of these catalysts and report here our results. In particular, we provide DRIFT spectroscopic evidence that these polynuclear catalyst precursors are supported on MAO-treated silica intact.

2. Experimental

2.1. General data

All operations were carried out on a standard high vacuum line or in a dry-box under inert atmosphere. Toluene, diethyl ether, and benzene, were reagent grade, distilled from the appropriate drying agents under Ar atmosphere. Tri-iso-butylaluminum (Aldrich), MAO (10% toluene, Aldrich) and $LiAlH_4$ (1 M, Et_2O, Aldrich) were used as purchased. The compounds $(n\text{-}BuCp)_2ZrCl_2$ [8] and $(TMSCp)_2ZrCl_2$ [9] were prepared by literature methods.

Polymer molecular weights were determined by gel permeation chromatography using a Waters 150-C chromatograph eluting with 1,2,4-tricholorobenzene at 135 °C. Narrow MWD polystyrene standards were used for GPC calibration.

For GPC analyses conducted at the University of Akron, a 3-angle, miniDAWN-HT light scattering detector was used for absolute molar mass determination along with the same instrumentation, solvent and protocol. Please see ref. [10] for a discussion of molar mass distributions measured in this manner – they are invariably too narrow due to an *upward* (and spurious) trend in MW indicated by light-scattering at long elution volumes with polydisperse polyolefin samples.

2.2. Synthesis of $Cp_2ZrH_3AlH_2$ complexes [Cp = TMSCp, ^{n}BuCp]

Complexes $(TMSCp)_2ZrH_3AlH_2$ and $(n\text{-}BuCp)_2ZrH_3AlH_2$ were synthesized using the methods reported by Stephan and coworkers [5b,c] varying the solvent and temperature of reaction.

2.3. Preparation of $^nBuCp_2ZrH_3AlH_2$

A suspension of $(nBuCp)_2ZrCl_2$ (1.3 g, 3.2 mmoles) in 20 mL of ether was prepared in a 100 mL Schlenk flask under Ar. A solution of $LiAlH_4$ in ether (1.01 M, 7.0 mL 7.07 mmoles) was added slowly at 0 °C via syringe. After 30 min at 0 °C, the mixture was filtered to remove LiCl and excess $LiAlH_4$ and the filtrate concentrated to dryness *in vacuo* to provide crude product in quantitative yield. The crude product was extracted into toluene, filtered, and the filtrate concentrated to dryness *in vacuo* to provide material that was free of diethyl ether, as a white, air-sensitive powder, that was sparingly soluble in common organic solvents; a satisfactory combustion analysis was not obtained. FT-IR (Nujol) 3090 (Cp-H), 1820 (s, br, AlH_t), 1560 (s, ZrH_t), 1330 (br, $ZrH_{br}Al$), 1260, 1100, 1040 cm^{-1}. ^1H NMR (300 MHz, o-DCB-d_4, −55 °C) δ 5.95 (m, 2H, Cp), 5.90 (m, 2H, Cp), 5.84 (m, 2H, Cp), 5.74 (m, 2H, Cp), 3.60 (br m, 2H, AlH_2), 2.77 (t, 4H, $CpC\mathit{H_2}{}^{n}Pr$), 1.71 (m, 4H, $CpCH_2(C\mathit{H_2})_2Me$), 1.50 (m, 4H, $CpCH_2(C\mathit{H_2})_2Me$), 1.11 (t, 6H, $CpCH_2(CH_2)_2\mathit{Me}$), −1.34 (br m, H, ZrH_2Al), −1.97 (br m, H, ZrH_2Al). The signal due to Zr-H_t was obscured by residual protonated solvent in these spectra.

3. Preparation of silica supports

3.1. Thermal treatment

Thirty to 40 g of silica gel was weighed into a porcelain crucible and heated in a muffle furnace at 800 °C for 6 h. After this, it was transferred to a 250 mL Schlenk vessel and cooled *in vacuo* for a further 8 h.

In the case of PQ silica, a 60 × 4 cm glass column was packed with silica and heated in a tube furnace to 600 °C under vacuum for 2 h. It was then exposed to a flow of oxygen for 3 h at 600 °C and then cooled under a stream of N_2 to room temperature. It was stored in a glove-box prior to use.

3.2. Modification of silica gel with MAO

Dehydroxylated silica (5 g) was placed in a 250 mL Schlenk flask, and suspended in 50 mL of toluene under Ar. A solution of MAO in toluene (22 mL of 10 wt%, 33 mmol MAO) was added slowly at 0 °C with stirring. Alter the addition was complete, the suspension was warmed to 25 °C and stirred for 6 h at this temperature. The silica was then filtered through a medium frit and washed three times with anhydrous toluene to remove excess MAO. It was then dried *in vacuo* to provide a white, granular powder which turned yellow-brown when exposed to air.

A similar procedure was used for PQ silica using 1 g of silica suspended in 10 mL of toluene and adding 15 mL of 10 wt% MAO solution. After adding the MAO solution at 0 °C, the mixture was heated to 50 °C for 2 h, and then stirred at 25 °C for an additional 3 h before filtering and drying as above.

3.3. Impregnation of MAO modified silica gel with $^nBuCp_2ZrH_3AlH_2$

A freshly prepared sample of $^nBuCp_2ZrH_3AlH_2$ (40 mg, 0.11 mmol, corresponding to ca. 5 wt% Zr) was dissolved in toluene solution and added to a suspension of MAO modified silica gel (2 g) in toluene at 0 °C under Ar. The suspension was warmed to 25 °C and stirred for 6 h under Ar. The supported catalyst was filtered under Ar and washed three times with dry toluene and dried *in vacuo* to provide a pink-colored powder, which turned pale yellow on exposure to air. The percentages of Zr and Al of the supported catalysts were determined by atomic absorption spectroscopy or by ICP analysis. A typical ICP analysis (Table 1, entry 6) is reported below: