



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

Rogelio Charles^{a,b}, Rebeca González-Hernández^a, Elsa Morales^a,
Javier Revilla^b, Luis E. Elizalde^a, Gregorio Cadenas^a,
Odilia Pérez-Camacho^{a,**}, Scott Collins^{c,*}

^a Centro de Investigación en Química Aplicada, Saltillo, Coahuila, Mexico

^b Centro de Investigación y Desarrollo Tecnológico, Lerma, Edo. de México, Mexico

^c Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, United States

ARTICLE INFO

Article history:

Received 13 November 2008

Received in revised form 12 January 2009

Accepted 10 March 2009

Available online 24 March 2009

Keywords:

Polymerization

Metallocene

Supported

DRIFT

Aluminohydride

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.

© 2009 Elsevier B.V. All rights reserved.

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].

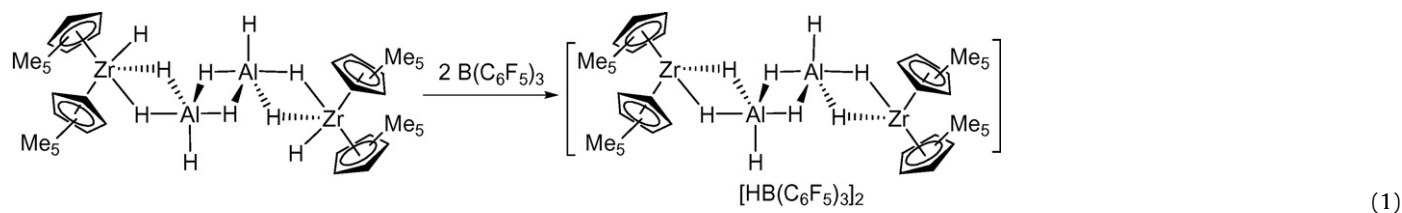
In contrast, less work has been focused on the use of metallocene dialkyls or related compounds as supported catalyst precursors, despite the generally higher chemoselectivity such complexes exhibit on reaction with hydroxylated supports (i.e. exclusive reaction at the Zr-R bond [3]) and the ease with 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 (generally $Cp_2ZrH_3AlH_2$ [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)).

* Corresponding author. Tel.: +1 330 972 7259; fax: +1 330 972 5290.

** Corresponding author.

E-mail addresses: odilia@ciqa.mx (O. Pérez-Camacho), collins@uakron.edu (S. Collins).



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 LiAlH₄ (1 M, Et₂O, Aldrich) were used as purchased. The compounds (n-BuCp)₂ZrCl₂ [8] and (TMSCp)₂ZrCl₂ [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-trichlorobenzene 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 Cp₂ZrH₃AlH₂ complexes [Cp = TMSCp, ⁿBuCp]

Complexes (TMSCp)₂ZrH₃AlH₂ and (n-BuCp)₂ZrH₃AlH₂ were synthesized using the methods reported by Stephan and co-workers [5b,c] varying the solvent and temperature of reaction.

2.3. Preparation of ⁿBuCp₂ZrH₃AlH₂

A suspension of (n-BuCp)₂ZrCl₂ (1.3 g, 3.2 mmoles) in 20 mL of ether was prepared in a 100 mL Schlenk flask under Ar. A solution of LiAlH₄ 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 LiAlH₄ 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-d₄, -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, AlH₂), 2.77 (t, 4H, CpCH₂ⁿPr), 1.71 (m, 4H, CpCH₂(CH₂)₂Me), 1.50 (m, 4H, CpCH₂(CH₂)₂Me), 1.11 (t, 6H, CpCH₂(CH₂)₂Me), -1.34 (br m, H, ZrH₂Al), -1.97 (br m, H, ZrH₂Al). 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 N₂ 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. After 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 ⁿBuCp₂ZrH₃AlH₂

A freshly prepared sample of ⁿBuCp₂ZrH₃AlH₂ (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:

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O	P ₂ O ₅	ZrO ₂
wt%	88.5	8.37	0.04	0.21	<0.01	0.03	0.19	<0.01	<0.01	0.31
wt% Al = 8.37 × [(2 × 26.98)/(2 × 26.98 + 3 × 15.995)] – 0.23 × (26.98/91.22) = 4.36										wt% Zr = 0.23

3.4. Catalyst characterization by DRIFT spectroscopy

The supported catalysts were analyzed as powders in a DRIFT accessory, equipped with sampling cups, under an inert atmosphere. The spectra were recorded at room temperature using a Nicolet Magna 500 FTIR spectrometer, by co-adding 50 scans at a resolution of 1 cm⁻¹. The spectral range was restricted to 4000–600 cm⁻¹. The spectra were collected in reflectance mode and the interferogram transformed using the Kubelka–Munk algorithm. The DRIFT spectra depicted in Fig. 2 have been base-line corrected using a polynomial fit.

3.5. Polymerization procedure—activation with MAO

The supported or soluble catalysts were activated using 5.0 mL of a 10 wt% solution of MAO in toluene (7.54 mmol of MAO), and in all the cases the solutions and suspensions were transferred by gas-tight 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 h to 90 °C with AlEt₃/toluene to remove all moisture traces.

Polymerization conditions for all the runs were: ethylene pressure of 3.9 bar, 200 mL of *i*-octane, 4.0 mL of a 13 wt% solution of MMAO (modified methylaluminoxane: an aliphatic hydrocarbon soluble aluminoxane formed by hydrolysis of a mixture of AlMe₃ and TIBAL) in isoParE (Akzo-Nobel) and polymerization temperatures of 25, 50 or 75 °C. The monomer flow rate was continually

monitored through the mass flow meter and polymerizations were carried out for 30 min.

The polymerization was stopped by rapid depressurization 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 h. Melting temperatures were between 133 and 137 °C indicating the formation of high density poly(ethylene).

4. Leaching experiments

For the catalyst leaching experiments, the supported catalyst (~50 mg, 8.1 μmol of Zr), and co-catalyst MAO (6.7 mL, 10 wt% solution in toluene, Al:Zr = 1000) were stirred in a 100 mL Schlenk flask at room temperature under Ar atmosphere, for 10 min. The mixture was added by syringe, to an addition burette connected to the polymerization reactor, through a stainless steel filter (7 μ). The burette was pressurized to 5.1 bar under N₂, and the catalyst was delivered to the polymerization reactor with a continuous flow of ethylene in the presence of hydrogen (total *p* = 3.9 bar, C₂:H₂ = 8:1) at 70 °C for 1 h. The results are as follows:

Cat (g)	Filtered	PE (g)	Activity ^a	M _w	M _w /M _n
0.057	No	23.5	2.7	7560	1.9
0.053	Yes	14.4	1.8	8040	1.8

^a 10⁶ g PE/mol Zr × h.

Table 1
Ethylene polymerization using soluble and supported aluminohydride complexes^a.

Entry	Support ^b	Catalyst	Al (wt%) ^c	Zr (wt%) ^c	Al:Zr ^d	Zr (μmol)	Al:Zr ^e (10 ³)	T (°C)	A ^f	M _w (kg mol ⁻¹)	PDI
1	–	nBuCp ₂ ZrH ₃ AlH ₂ /MAO	–	–	–	6.0	1.2	50	16.5	511	3.6
2	–	nBuCp ₂ ZrCl ₂ /MAO	–	–	–	8.5	0.89	50	11.0	275	3.5
3	–	nBuCp ₂ ZrH ₃ AlH ₂ /MAO	–	–	–	6.0	1.2	75	24.0	91	2.3
4	–	nBuCp ₂ ZrCl ₂ /MAO	–	–	–	8.5	0.89	75	14.1	71	2.5
5	DS-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	4.4	0.025	598	0.18	41	50	7.35	142	2.4
6	DS-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	4.4	0.23	65.2	1.71	4.4	50	2.58	243	4.0
7	DS-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	4.4	0.95	15.7	2.55	3.0	^g	–	–	–
8	DS-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂ ^h	4.4	0.076 ⁱ	197	0.20	38	50	31.2	457	3.5
9	DS-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂ ^h	4.4	0.076 ⁱ	197	0.14	54	50	34.6	203	1.5
10	DS-SiO ₂ /MAO	nBuCp ₂ ZrCl ₂	4.4	0.072	205	0.71	11	50	26.0	267	2.6
11	DS-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂ ^h	4.4	0.076 ⁱ	197	0.30	25	75	52.8	91	1.3
12	DS-SiO ₂ /MAO	nBuCp ₂ ZrCl ₂	4.4	0.072	205	0.46	16	75	42.6	79	2.3
13	PQ-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	14.5	0.33	148	1.78	2.3 ^j	60	29.9	143	1.5
14	PQ-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	14.5	2.98	16.4	16.3	0.25 ^j	60	2.05	160	1.5
15	PQ-SiO ₂ /MAO	nBuCp ₂ ZrCl ₂	14.5	0.57	86.0	3.12	1.3 ^j	60	15.3	148	1.5
16	PQ-SiO ₂ /MAO	nBuCp ₂ ZrCl ₂	14.5	1.67	29.4	9.15	0.45 ^j	60	2.89	154	1.6
17	PQ-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	14.5	0.37	132	2.03	3.7	50	2.03	417	4.1
18	PQ-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	14.5	0.39	126	2.14	3.5	50	3.28	234	3.4
19	PQ-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	14.5	0.59	83.1	3.23	2.3	50	4.12	264	3.6
20	PQ-SiO ₂ /MAO	nBuCp ₂ ZrH ₃ AlH ₂	14.5	1.71	28.7	9.37	0.80	50	3.31	165	4.0
21	–	TMSCp ₂ ZrH ₃ AlH ₂ /MAO	–	–	–	1.60	5.0	75	56.3	51.5	3.1
22	PQ-SiO ₂ /MAO	TMSCp ₂ ZrH ₃ AlH ₂	14.5	2.40	20.5	16.2	0.40	70	0.40	98.3	2.0
23	PQ-SiO ₂ /MAO	TMSCp ₂ ZrH ₃ AlH ₂	14.5	2.40	20.5	15.4	0.40	70	0.54	84.6	2.7
24	PQ-SiO ₂ /MAO	TMSCp ₂ ZrH ₃ AlH ₂	14.5	2.40	20.5	12.3	5.5	70	0.50	175	2.7

^a Polymerizations were conducted in 200 mL of iso-octane solution, using 4.0 mL of 13 wt% MMAO in isoParE as scavenger, for 30 min with P_{C₂H₄} = 3.9 bar unless otherwise noted.

^b Supports: DS-SiO₂/MAO = Davisil silica treated with MAO. PQ-SiO₂/MAO = PQ silica treated with MAO.

^c Zr and Al content were determined by atomic absorption or ICP analysis.

^d Surface Al:Zr ratio.

^e Solution Al:Zr ratio is based on the ratio of additional MAO to Zr used to activate the catalyst, prior to delivery to the reactor – see text for discussion.

^f Activity in 10⁶ g PE/mol Zr × h.

^g This reaction was strongly exothermic and was shut down after a few minutes.

^h This catalyst was prepared by stirring together 0.92 g of DS-SiO₂/MAO (4.4 wt% Al) with 0.08 g of the supported catalyst with the composition reported in entry 7.

ⁱ Calculated value based on dilution.

^j Polymerizations were conducted in hexane solution, using TIBAL as scavenger, for 30 min at P_{C₂H₄} = 7.9 bar.

4.1. Polymerization procedure—TIBAL as scavenger

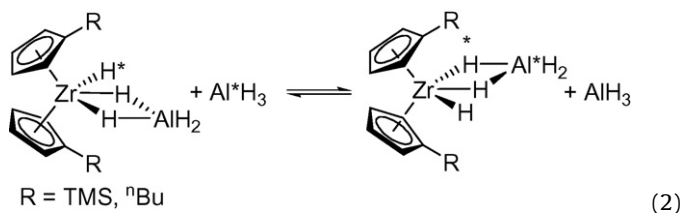
A 1.0 L Zipperclave™ reactor was heated to 100 °C under N₂ and kept under a flow of N₂ for 30 min at that temperature. It was evacuated and refilled five times with N₂ at 100 °C and then cooled to 25 °C under N₂ pressure.

After venting the reactor, TIBAL (0.814 g, 4.1 mmol) was delivered to the reactor using a 50.0 mL stainless steel sample vessel, flushing the contents with 300 mL of dry hexane into the reactor under an over-pressure of N₂. The resulting solution was heated to 60 °C and then stirred under 7.9 bar of ethylene at 1000 rpm until the temperature had stabilized at 60 °C and the flow of ethylene, as measured by a calibrated mass flow meter, had ceased (typically 30 min).

A suspension of 0.050–0.100 g of the supported catalyst in 20 mL hexane in a second sample vessel, was flushed into the reactor, using an additional 30 mL of hexane, under 8.6 bar of N₂. Polymerization was allowed to proceed for 30 min, and then the reaction was then quenched with a small volume of iPrOH. The reactor was cooled to 25 °C, vented and the polyethylene recovered by filtration, washing with MeOH. Polymer samples were dried in a vacuum oven at –1.0 bar at 60 °C for 6 h prior to analysis.

5. Results and discussion

Two types of metallocene complexes were investigated: ⁿBuCp₂ZrCl₂ and Me₃SiCp₂ZrCl₂. Both of these were converted to the corresponding aluminohydride complexes on treatment with LiAlH₄ in ether followed by extraction into toluene and drying. ⁿBuCp₂ZrH₃AlH₂ has not been reported before; it is likely this compound is not discrete but consists of a fluxional mixture of complexes differing in their nuclearity. In the case of Me₃SiCp₂ZrH₃AlH₂, this compound is known to exist in the solid state as a mixture of trinuclear Zr₂Al and tetranuclear Zr₃Al complexes [5b]. We suspect a similar formulation applies to ⁿBuCp₂ZrH₃AlH₂ based on the similarity in their low temperature ¹H NMR spectra where the exchange process depicted in Eq. (2) is slow on the NMR time scale [6].



Supported catalysts were prepared from two different grades of silica—a broad particle size distribution silica (70–230 mesh) provided by Aldrich Chemical Co., equivalent to Davisil™ 635 ($\phi = 60$ Å, 500 m²/g, 0.75 mL/g), that was fully dehydroxylated at 800 °C and a high pore volume, spherical PQ silica (MS-3040, $\phi = 310$ Å, 420 m²/g, 3.2 mL/g) that was partially dehydroxylated at 600 °C.

In each case the silica was treated with excess MAO in toluene solution, followed by washing and drying. In the case of PQ silica, significantly more MAO could be impregnated into the pores of this material (14.5 wt% Al by atomic absorption analysis) compared with the more commonly available Davisil™ silica (4.4 wt%).

The supported catalysts were prepared by suspending the alumoxane-impregnated silica supports with a metallocene dichloride or aluminohydride formulation in toluene slurry, followed by filtration and drying. The supported catalysts were analyzed for Zr and Al and the compositions prepared are summarized in Table 1.

Fig. 1 compares the morphologies and distribution of Zr as measured by SEM and SEM/EDX, respectively for the two silicas used. It can be observed that the spherical PQ silica has a much more even

distribution and higher amount of Zr supported than the irregular Davisil™ silica.

Catalysts prepared from Davisil™ silica (DS-SiO₂) featured somewhat lower surface Al:Zr ratios at comparable Zr content (e.g. Table 1 entry 6 vs. 13). On the other hand the MAO-treated, PQ silica (PQ-SiO₂) absorbed significantly higher amounts of metallocene at the highest loadings investigated (entry 7 vs. 14) but both supports feature equivalent Al:Zr ratios of ca. 16:1. Under these conditions, it can be expected that a significant portion of the supported metallocene is not in its most active state and in the case of the dichloride precursors, alkylation/ionization may even be incomplete [11].

Some of the supported catalysts prepared were characterized by diffuse reflectance FT-IR (DRIFT) spectroscopy. Shown in Fig. 2 is the DRIFT spectra of MAO-treated silica, and the supported ⁿBuCp₂ZrH₃AlH₂ catalyst prepared from it. Characteristic signals due to terminal Al-H, Zr-H and bridging Zr-H-Al stretches are expected in the 1700–1900, 1500–1600 and 1200–1400 cm⁻¹ regions, respectively [5d,5h, 12]. In particular, the peak at 1880 cm⁻¹ is consistent with terminal Al-H stretching, while that at 1290 cm⁻¹ could be due to Zr-H-Al and/or Al-H-Al stretching. A weaker absorption is observed at 1470 cm⁻¹ which might be assigned to terminal Zr-H stretching though generally in neutral complexes of this type this absorption is typically found at $\bar{\nu} > 1500$ cm⁻¹. In support of the first two assignments, in the DRIFT spectrum of a supported catalyst which was exposed to air (red to yellow color change), the two bands at 1880 and 1290 cm⁻¹ are noticeably reduced in intensity.

For comparison purposes, the solid state FT-IR spectrum (Nujol mull) of ⁿBuCp₂ZrH₃AlH₂ in Fig. 2 exhibits terminal Al-H, and Zr-H stretching at 1820 and 1560 cm⁻¹ and bridging Zr-H-Al stretching at 1330 cm⁻¹ respectively. That the 1820 cm⁻¹ absorbance shifts markedly on contact with MAO silica and the 1560 cm⁻¹ absorption is absent¹ is not unexpected. In particular, if ionization of these complexes by MAO is at all similar to B(C₆F₅)₃ (Eq. (1)) one would not expect to see signals due to terminal Zr-H stretching in these supported catalysts.

Table 1 summarizes the polymerizations results. In all experiments where excess MAO was used as an activator (entries 1–12 and 17–24), the soluble or supported catalyst was pre-contacted with 5.0 mL of a 7.0 wt% (w:v) solution of MAO in toluene for 5–10 min prior to injection of the mixture into the autoclave reactor. Since this procedure can cause leaching of the supported catalyst from the support [13], particularly any unactivated, or neutral metallocene complex present, the results summarized in Table 1 must be discussed with this knowledge in mind. Further, in these cases, an additional amount of MMAO was present in the iso-octane solution and this will also exacerbate leaching, particularly at elevated T.

A control experiment featuring pre-contacting a supported ⁿBuCp₂ZrH₃AlH₂ catalyst (Zr = 1.39 wt%) with MAO (total Al:Zr = 1000:1) followed by filtration through a 7 μ frit into the reactor under these conditions, revealed that about 2/3 of the observed activity can be accounted for by leaching during this pre-contacting period. As might be expected, the MW and MWD of the PE formed in both cases (filtered vs. unfiltered) was essentially identical (see Section 2).

Most polymerization experiments were conducted without prior knowledge as to the actual amount of Zr on the support and therefore many experiments with the supported catalysts feature large and variable Al:Zr ratios as a fixed quantity of MAO (*vide supra*) and supported catalyst (generally 0.02–0.06 g) was used. On the other hand when Al:Zr ratios were varied between 400:1

¹ An absorption at ca. 1640 cm⁻¹ of variable intensity appears in all three DRIFT spectra in Fig. 2. Evidently this is not due to a metallocene compound.

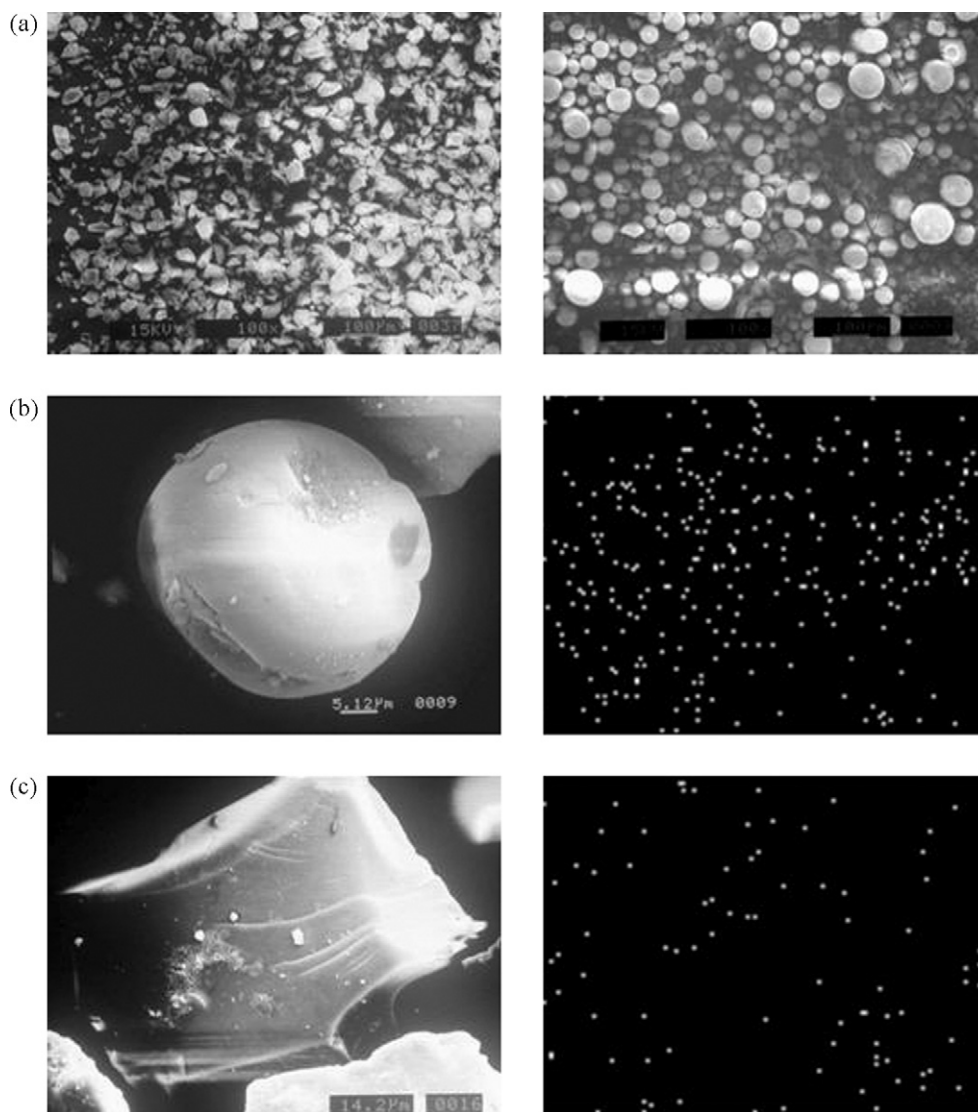


Fig. 1. (a) SEM of Davisil™ and PQ silicas prior to modification. SEM of (b) PQ and (c) Davisil™ silicas after modification with MAO and $n\text{BuCp}_2\text{ZrH}_3\text{AlH}_2$; Zr distribution as measured by EDX.

and 5500:1 using a $\text{TMSCp}_2\text{ZrH}_3\text{AlH}_2$ supported catalyst of known (and identical) composition, the activities observed were largely independent of this ratio (entries 22–24).

Entries 5–7 demonstrate the effect of increasing the amount of Zr on the support. Though activity based on Zr declines as the amount of Zr is increased, the actual yield of polymer increases dramatically and to the point where isothermal conditions could not be maintained at the highest catalyst loading (entry 7).

For this reason, subsequent experiments were conducted with this catalyst but it was first diluted by mixing with additional SiO_2 -MAO using magnetic stirring. This undoubtedly destroys any particle morphology initially present and may increase surface area but the net result of this treatment was enhanced activity (ca. 4–5 \times higher) at comparable Zr loadings (compare entry 5 vs. 8).

Entries 8–12 compare the performance of this aluminohydride catalyst vs. the dichloride catalyst prepared with similar compositions and in the same manner. Polymerization activity based on Zr is anywhere from 25 to 35% higher using the aluminohydride catalysts. Very little difference in MW is observed as a function of supported catalyst used at 75 °C (entries 11–12). This is similar to what is observed in solution using these two different catalyst

precursors (entries 3–4 – see also ref. [6]). At lower T , a distinct difference in MW is seen (entries 1–2) and this is mirrored to some extent using a supported catalyst though there is significant variation in the results (entries 8 vs. 9 and 8, 9 vs. 10).

Entries 13–16 compare the two different catalyst precursors at two different Zr loadings using the higher pore volume PQ silica. Here MAO was not used to (pre)activate these catalysts and TIBAL was used as a scavenger – catalyst leaching is less problematic and one is now comparing intrinsic activities. As one might expect, those catalysts which feature lower Zr loadings have much higher activities (based on Zr) since more of the catalyst precursor is activated on the support. In fact the relationship between catalyst activity and surface Al:Zr ratio is linear and independent of the nature of the catalyst precursor (Fig. 3).

Under these conditions there were limited if any differences between polymer MW vs. catalyst precursor; the narrower MWD reported reflect the fact that a 3-angle light-scattering detector was used for these GPC analyses (see Section 2).

Entries 17–20 examine the effect of changing the surface Al:Zr ratio using PQ-silica supported ${}^n\text{BuCp}_2\text{ZrH}_3\text{AlH}_2$ but featuring MAO activation. As one might expect, there is no effect of surface Al:Zr ratio seen here on either catalyst activity or polymer

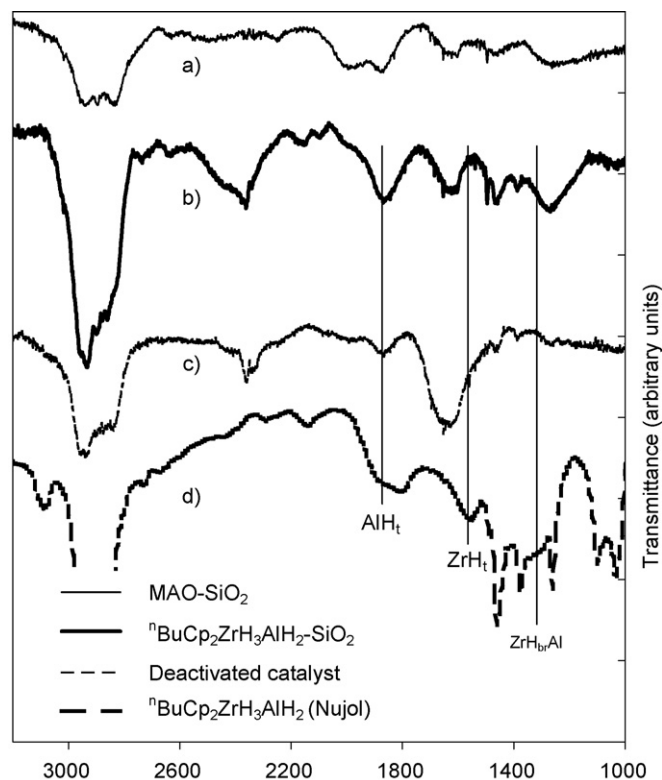


Fig. 2. DRIFT spectra of (a) MAO-treated silica (dehydroxylated silica as background), (b) $n\text{BuCp}_2\text{ZrH}_3\text{AlH}_2$ supported on MAO-silica ($\text{Zr} = 1.39 \text{ wt}\%$) and (c) $n\text{BuCp}_2\text{ZrH}_3\text{AlH}_2$ supported catalyst ($\text{Zr} = 1.97 \text{ wt}\%$) after exposure to air; MAO-treated silica was used as a background in both cases. d) Transmission FT-IR spectrum of $n\text{BuCp}_2\text{ZrH}_3\text{AlH}_2$ (Nujol mull) with assignments indicated.

MW since much of the observed polymerization activity probably results from catalyst leaching during or subsequent to the activation period.

Finally, entries 21 and 22–24 compare the performance of soluble and supported $\text{TMSCp}_2\text{ZrH}_3\text{AlH}_2$ catalysts on activation with MAO. The supported catalyst is much less active than the soluble version though the MW of the polymer formed is significantly higher than that obtained with the homogeneous catalyst and sensitive to the Al:Zr ratio. It could be that this more sterically hindered, catalyst precursor is less sensitive to leaching by additional MAO. We do note that another sample of this supported catalyst, which featured a lower catalyst loading, had much higher activity ($\text{Zr} = 1.59 \text{ wt}\%$, $A = 6.6 \times 10^6 \text{ g PE/mol Zr} \times \text{h}$ at 3.9 bar, 50°C) so catalyst activation may also be influenced here.

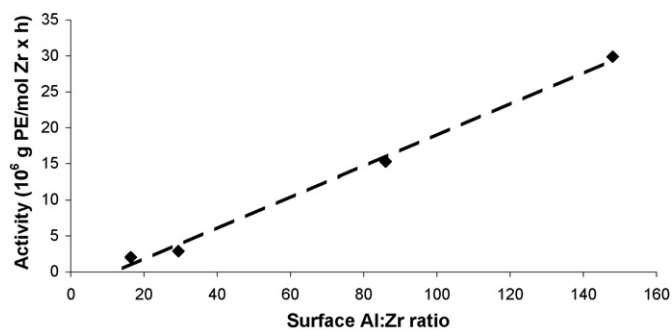


Fig. 3. Plot of polymerization activity (Conditions: TIBAL, hexane, 60°C , 30 min, 7.9 bar C_2H_4) vs. surface Al:Zr ratio for metallocene catalysts supported on MAO-treated PQ silica.

6. Conclusions

This work has demonstrated that aluminohydride complexes of zirconocenes can be supported on MAO-treated silica and that these supported catalysts can exhibit superior activity compared with their dichloride analogues when activated by additional MAO. Spectroscopic data provide evidence that these polynuclear complexes are deposited intact on MAO-modified silica. It is likely that the improved activity of the aluminohydride catalysts is due to enhanced leaching of the polynuclear catalyst from the support by MAO since polymerization reactions with these same catalysts in the presence of TIBAL do not show similar behavior. Our studies highlight the key role of surface Al:Zr ratios in affecting supported catalyst performance in the absence of significant catalyst leaching.

Acknowledgements

The authors would like to thank the University of Akron for financial support of this work and NOVA Chemicals Corporation and PQ Corporation for donation of the PQ silica. In addition, R.G.H. and R.C. acknowledge the financial support of CONACYT for doctoral fellowships and travel funds to visit the University of Akron. We also thank Maricela García, Víctor Comparán, and Alejandro Espinoza for technical support at CIQA.

References

- Recent reviews:
 - G. Fink, H.-H. Brintzinger, *Metal-Catal. Ind. Org. Proc.* (2006) 218–254;
 - J.R. Severn, J.C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* 105 (2005) 4073–4147;
 - H.G. Alt, *Dalton Trans.* (2005) 3271–3276;
 - D.-H. Lee, *Polymer (Korea)* 29 (2005) 321–330;
 - S.I. Woo, H.Y. Cho, L. Cui, N.H. Tarte, D.S. Hong, *Curr. Trends Polym. Sci.* 9 (2004) 99–107.
- G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla, B. Tesche, *Chem. Rev.* 100 (2000) 1377–1390;
 - G.G. Hlatky, *Chem. Rev.* 100 (2000) 1347–1376.
- N. Millot, S. Soignier, C.C. Santini, A. Baudouin, J.-M. Basset, *J. Am. Chem. Soc.* 128 (2006) 9361–9370;
 - V.N. Panchenko, V.A. Zakharov, E.A. Paukshtis, *J. Mol. Cat. A: Chem.* 240 (2005) 33–39;
 - C.P. Nicholas, T.J. Marks, *Langmuir* 20 (2004) 9456–9462;
 - C.P. Nicholas, H. Ahn, T.J. Marks, *J. Am. Chem. Soc.* 125 (2003) 4325–4331;
 - R.A. Metcalfe, D.I. Kreller, J. Tian, H. Kim, N.J. Taylor, J.F. Corrigan, S. Collins, *Organometallics* 21 (2002) 1719–1726;
 - M. Jezequel, V. Dufaud, M.J. Ruiz-Garcia, F. Carrillo-Hermosilla, U. Neugebauer, G.P. Nicolai, F. Lefebvre, F. Bayard, J. Corker, S. Fiddy, J. Evans, J.-P. Broeyer, J. Malinge, J.-M. Basset, *J. Am. Chem. Soc.* 123 (2001) 3520–3540;
 - J. Tian, S. Wang, Y. Feng, J. Li, S. Collins, *J. Mol. Cat. A: Chem.* 144 (1999) 137–150;
 - G.G. Hlatky, D.J. Upton, *Macromolecules* 29 (1996) 8019–8020.
- Welborn, H.C.Jr., *Eur. Pat. Appl. EP 206794* (1986), 24 pp.
- A.I. Sizov, T.M. Zvukova, V.K. Belsky, B.M. Bulychiev, *J. Organomet. Chem.* 619 (2001) 36–42;
 - N. Etkin, D.W. Stephan, *Organometallics* 17 (1998) 763–765;
 - N. Etkin, A.J. Hoskin, D.W. Stephan, *J. Am. Chem. Soc.* 119 (1997) 11420–11421;
 - K. Khan, C.L. Raston, J.E. McGrady, B.W. Skelton, A.H. White, *Organometallics* 16 (1997) 3252–3254;
 - B.M. Bulychiev, *Polyhedron* 9 (1990) 387–408;
 - C.J. Carmalt, N.C. Norman, L.C. Clarkson, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 1, Pergamon Press, Oxford, UK, 1995, p. 545;
 - D.J. Cardin, M.F. Lappert, C.L. Raston, *Chemistry of Organo-Zirconium and -Hafnium Compounds*, Ellis Horwood, Chichester, UK, 1986, Chapter 20;
 - P.C. Wailes, H. Weigold, *J. Organomet. Chem.* 24 (1970) 405–411;
 - B. Kautzner, P.C. Wailes, H. Weigold, *Chem. Commun.* (1969) 1105.
- R. Gonzalez-Hernandez, J. Chai, R. Charles, O. Perez-Camacho, S. Kniajanski, S. Collins, *Organometallics* 25 (2006) 5366–5373.
- (a) N. Guo, C.L. Stern, T.J. Marks, *J. Am. Chem. Soc.* 130 (2008) 2246–2261;
 - M.R. Salata, T.J. Marks, *J. Am. Chem. Soc.* 130 (2008) 12–13;
 - H. Li, L. Li, D.J. Schwartz, M.V. Metz, T.J. Marks, L. Liable-Sands, A.L. Rheingold, *J. Am. Chem. Soc.* 127 (2005) 14756–14768;
 - H. Li, C.L. Stern, T.J. Marks, *Macromolecules* 38 (2005) 9015–9027;
 - H. Li, L. Li, T.J. Marks, *Angew. Chem., Int.* 43 (2004) 4937–4940;
 - H. Li, L. Li, T.J. Marks, L. Liable-Sands, A.L. Rheingold, *J. Am. Chem. Soc.* 125 (2003) 10788–10789;

- (g) L. Li, M.V. Metz, H. Li, M.-C. Chen, T.J. Marks, L. Liable-Sands, A.L. Rheingold, *J. Am. Chem. Soc.* 124 (2002) 12725–12741.
- [8] (a) R.A. Newmark, L.D. Boardman, A.R. Siedle, *Inorg. Chem.* 30 (1991) 853–856;
(b) J.H. Davis, H.-N. Sun, D. Redfield, G.D. Stucky, *J. Magn. Reson.* 37 (1980) 441–448.
- [9] M.F. Lappert, P.I. Riley, P.I.W. Yarrow, J.L. Atwood, W.E. Hunter, M.J. Zaworotko, *J. Chem. Soc. Dalton Trans.* (1981) 814–821.
- [10] R.A. Stapleton, J. Chai, A. Nuanthanom, Z. Flisak, M. Nele, T. Ziegler, P.L. Rinaldi, J.B.P. Soares, S. Collins, *Macromolecules* 40 (2007) 2993–3004.
- [11] (a) D.E. Babushkin, C. Naundorf, H.-H. Brintzinger, *Dalton Trans.* (2006) 4539–4544;
(b) U. Wieser, F. Schaper, H.-H. Brintzinger, *Macromol. Symp.* 236 (2006) 63–68;
(c) D.E. Babushkin, H.-H. Brintzinger, *J. Am. Chem. Soc.* 124 (2002) 12869–12873.
- [12] (a) A.I. Sizov, T.M. Zvukova, A.V. Khvostov, V.K. Belsky, A.I. Stash, B.M. Bulychev, *J. Organomet. Chem.* 681 (1–2) (2003) 167–173;
(b) R.J. Wehmschulte, P.P. Power, *Polyhedron* 18 (1999) 1885–1888.
- [13] See ref. [3g];
(a) J. Tian, Y.-S. Ko, R.A. Metcalfe, Y. Feng, S. Collins, *Macromolecules* 34 (2001) 3120–3122;
(b) D. Harrison, I.M. Coulter, S. Wang, S. Nistala, B.A. Kuntz, M. Pigeon, J. Tian, S. Collins, *J. Mol. Cat. A: Chem.* 128 (1998) 65–77.