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Polymerization of Propylene Using Supported, Chiral, *ansa*-Metallocene Catalysts: Production of Polypropylene with Narrow Molecular Weight Distributions[1a]

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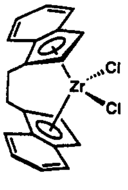
ABSTRACT: The chiral *ansa*-metallocenes 1,2-ethylenebis(η^5-1-indenyl)- and 1,2-ethylenebis(η^5-1-tetrahydroindenyl)zirconium dichloride (1 and 2, respectively) can be supported on partially dehydroxylated SiO_2 and Al_2O_3, and these supported systems can be used to polymerize propylene in the presence of methylaluminoxane. The most active supported systems were derived from partially dehydroxylated SiO_2 or Al_2O_3 that had been pretreated with excess trimethylaluminum. The properties of the polypropylene produced are essentially indistinguishable from that produced under homogeneous conditions using these same catalysts.

Introduction

The discovery of homogeneous Ziegler–Natta catalysts, derived from metallocene compounds and methylaluminoxane cocatalyst, that combine high activity with excellent stereoregularity in the isotactic polymerization of α-olefins has led to a resurgence of interest in this field.[2] Metallocene catalysts that provide access to isotactic,[2g,i-k] isotactic-stereoblock,[2l] syndiotactic,[2h] and isotactic–atactic block[2d] polymers of propylene have been developed. A significant impediment to the commercialization of such catalytic systems is the cost reflected in the requirement that a very large excess of methylaluminoxane (MAO) must be employed to obtain high catalytic activity and catalyst stability.[2] One approach to overcome this problem that has met with some success, at least for ethylene polymerization, involves the preparation of cationic, d^0, 14 e^-, metallocene compounds which do not require a cocatalyst for polymerization.[3] Another approach, the results of which have been mainly disclosed in the patent literature,[4] has involved adsorbing an appropriate metallocene compound, with or without an aluminum alkyl, on silica, alumina, or other high surface area support[5] and using such systems for ethylene polymerization. In several cases, it is claimed that additional MAO is not required during polymerization if it is initially deposited or prepared on the surface.

As far as we are aware, these studies have been concerned with ethylene polymerization; there appear to have been few reports on propylene polymerization using supported versions of the well-studied ethylenebis(η^5-indenyl)- and ethylenebis(η^5-tetrahydroindenyl)zirconium dichloride catalysts (1 and 2, respectively).[6] In this paper, we describe the preparation of supported versions of these catalysts and their use in the polymerization of propylene.



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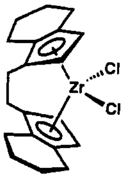

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Results

We have confined our study to supported systems prepared by adsorbing compounds 1 and 2 on commercially available silica (Aldrich, grade 62, 74–250-μm particle size) or γ-alumina (Vista, Catapal G, 65-μm average particle size) with surface areas of 300 and 150 m^2/g, respectively. The supports were freed of surface impurities, and fully hydroxylated, partially dehydroxylated, and dehydroxylated SiO_2 and Al_2O_3 (100% OH-S, PDS, DS and 100% OH-A, PDA, and DA, respectively) were prepared as described in the literature.[7] The hydroxyl group content was determined by titration with trimethylaluminum or methyllithium (Table I).[8] The latter method is expected to provide higher and more accurate values of hydroxyl content than the former.[9] The values reported in Table I are based on the stoichiometry shown in eq 1a.

$$\text{support–OH} + AlMe_3 \text{ (or MeLi)} \rightarrow \text{support–OAlMe}_2 \text{ (or support–OLi)} + CH_4 \quad (1a)$$

$$\text{support–OAlMe}_2 + 2CH_3OH \rightarrow \text{support–OAl(OCH}_3)_2 + 2CH_4 \quad (1b)$$

In addition to the above supports we also investigated the use of PDA and PDS that had been pretreated with $AlMe_3$ *prior* to adsorbing the metallocene compound (vide infra). To determine aluminum content, these treated supports were hydrolyzed and the methane evolved was measured. In both cases, the amount of $AlMe_3$ adsorbed, 0.087 ± 0.018 mol of Al/mol of PDA and 0.054 mol of Al/mol of PDS, based on the stoichiometry shown in eq 1b, corresponded closely to the theoretical amount predicted based on the hydroxyl surface content measured using $AlMe_3$ (Table I, entries 2 and 5).

The metallocenes were adsorbed on the oxide surface as described in the Experimental Section. The metallocene content of each of these supported systems was estimated by determining the amount of unadsorbed metallocene present, by UV–visible spectrophotometry, in the toluene solution used in their preparation and subtracting this value from the total amount of metallocene compound originally present. In addition, a C,H,Cl analysis of one of these supported catalysts was obtained, and the results were in agreement with that obtained using the former method (see Experimental Section). The data obtained for both compounds 1 and 2 are summarized in Table II.

As can be seen from the data in Table II, compound 1 is adsorbed in significantly higher amounts than compound 2 on all of the supports where both compounds were supported, despite being of similar surface area.[10a] In the case of partially dehydroxylated or fully hydroxylated

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Table I
Surface Hydroxyl Content of Silica and Alumina

entry	support[a]	titrant	mol of OH/mol of oxide[b]
1	DA	MeLi	0.031
		$AlMe_3$	0.018
2	PDA	MeLi	0.144
		$AlMe_3$	0.087
3	100% OH-A	MeLi	0.260
		$AlMe_3$	0.218
4	DS	MeLi	0.025
5	PDS	MeLi	0.078
		$AlMe_3$	0.054
6	100% OH-S	MeLi	0.112
		$AlMe_3$	0.078

[a] DA = dehydroxylated alumina; PDA = partially dehydroxylated alumina; 100% OH-A = fully hydroxylated alumina; DS = dehydroxylated silica; PDS = partially dehydroxylated silica; 100% OH-S = fully hydroxylated silica. For procedures employed to prepared the various supports, see ref 7. [b] Values quoted are the average of at least two separate determinations but are not corrected for the solubility of methane in ether or toluene; the error between determinations is <10%.

Table II
Metallocene Adsorption on Silica and Alumina

entry	support[a]	compd 1 (mmol/g)[b]	compd 2 (mmol/g)[b]
1	PDA–$AlMe_3$	0.101 ± 0.031	*c*
2	100% OH-A	0.198 ± 0.021	*c*
3	PDA	0.196 ± 0.016	0.083 ± 0.010
4	DA	0.204 ± 0.016	0.062
5	PDS–$AlMe_3$	0.077 ± 0.018	0.026 ± 0.005
6	100% OH-S	0.241 ± 0.023	*c*
7	PDS	0.161 ± 0.017	0.074
8	DS	0.168 ± 0.012	0.069 ± 0.010

[a] PDA–$AlMe_3$ = partially dehydroxylated alumina pretreated with $AlMe_3$; 100% OH-A = fully hydroxylated alumina; PDA = partially dehydroxylated alumina; DA = dehydroxylated alumina; PDS–$AlMe_3$ = partially dehydroxylated silica pretreated with $AlMe_3$; 100% OH-S = fully hydroxylated silica; PDS = partially dehydroxylated silica; DS = dehydroxylated silica. See Table I for degree of surface hydroxylation. [b] Amount of compound 1 or 2 supported was determined from the difference between the amount initially used in catalyst preparation and that present in the toluene-soluble portion following filtration and washing of the support (see text). [c] Not studied.

Table III
Polymerization of Propylene with Compound 1 Supported on Silica or Alumina in the Presence of Methylaluminoxane[a]

entry	support[b]	Zr (μmol)[c]	pC_3H_6 (atm)	*T* (°C)[d]	yield (g)	R_p[e]
1	PDA–$AlMe_3$	7.0	5	31–47	16.0	305
2	PDA	7.0	5	30–37	7.1	135
3	DA	8.7	5	30–38	1.0	15
4	100% OH-A	7.2	5	30–34	0.0	nil
5	PDS–$AlMe_3$	2.3	3	29–36	4.1	396
6	DS	7.0	5	28–36	1.9	36
7	PDS	6.6	5	29–36	0.5	10
8	100% OH-S	10.0	5	25–30	0.0	nil
9	none	7.0	1	25–37	16.3 ± 0.4	1550

[a] Polymerizations were conducted in a small autoclave without temperature control or efficient stirring and the conditions were as follows: 5.2 mmol of Al as MAO, reaction time 1.5 h, 100 mL of toluene. [b] PDA–$AlMe_3$ = partially dehydroxylated alumina pretreated with $AlMe_3$; PDA = partially dehydroxylated alumina; DA = dehydroxylated alumina; 100% OH-A = fully hydroxylated alumina; PDS–$AlMe_3$ = partially dehydroxylated silica pretreated with $AlMe_3$; DS = dehydroxylated silica; PDS = partially dehydroxylated silica; 100% OH-S = fully hydroxylated silica. See Tables I and II for degrees of hydroxylation and amount of metallocene compound adsorbed, respectively. [c] Calculated amount based on the data reported in Table II. [d] Observed temperature variation during monomer saturation and polymerization. [e] Average rate of polymerization in kg of PP/mol of Zr × h × atm.

supports, adsorption of compound 1 was accompanied by significant decomposition; the soluble filtrate contained, in addition to compound 1, bis(indenyl)ethane as revealed by ^1H NMR spectroscopy. Less decomposition was evident for the alumina supports than for silica. Significantly lower amounts of both compounds adsorb on PDS or PDA that has been pretreated with $AlMe_3$. In this case, decomposition of the metallocene was not observed. In all cases, the amounts adsorbed are less than would be predicted, based on monolayer coverage.[10b]

Compound 1 was adsorbed on each surface (see Experimental Section), and these supported catalysts, in the presence of MAO, were used to quickly screen for activity toward propylene (Table III). From these results it was concluded that compound 1, when supported on PDS or PDA that was pretreated with $AlMe_3$ prior to supporting the metallocene compound (Table III, entries 1 and 5), gave rise to the most active catalysts. The PDA- and DS-supported catalytic systems were also relatively active for propylene polymerization.

Since the PDA- and PDS-supported systems, especially those pretreated with $AlMe_3$, exhibited the most promise, they were investigated in more detail. It was determined (see Experimental Section) that the maximum amount of MAO that could be supported on PDA and PDS at room temperature was 12.5 mmol of Al/g of PDA and 10.5 mmol of Al/g of PDS, based on the formula weight of MAO (1114) determined previously by Sinn and co-workers.[11] Similar values have been reported recently for PDA and PDS.[12] In the case of the trimethylaluminum-treated supports, lower amounts of MAO could be supported: 8.8 mmol of Al/g of PDA–$AlMe_3$ and 6.9 mmol of Al/g of PDS–$AlMe_3$.

These results when combined with those summarized in Table II indicate that the *maximum* amount of MAO adsorbed under the polymerization conditions summarized in Table III corresponds to the following Al:Zr ratios: PDA (64:1), PDS (65:1), PDA–$AlMe_3$ (88:1), and PDS–$AlMe_3$ (89:1). In the case of the latter two supports, the maximum total concentration of bound aluminum to metallocene is not significantly different as the amount of additional aluminum present (as $OAlMe_2$) is small (vide supra). It will be appreciated that these ratios are considerably less than those commonly employed under homogeneous conditions for maximum activity[2] even though the total Al:Zr ratio in the polymerizations summarized in Table III was ~1000:1.

The results of a series of propylene polymerizations with the two metallocene compounds (1 and 2) supported on PDA or PDS that was pretreated with $AlMe_3$ at 30 °C in toluene solution (3.0 atm of propylene, 300 mg of MAO) are summarized in Table IV. In addition, polymerizations were also conducted under the same conditions using the unsupported (i.e., soluble) catalysts.

Several features are worth noting. First, the supported systems are less active polymerization catalysts than the soluble systems on a per metal basis. This is not surprising; one would expect lower activities due to irreversible deactivation of the metallocene compound during adsorption and/or inefficient production of active centers on the surface compared to in solution.

What is surprising is that the properties of the polymer produced are essentially unaffected when carrying out the polymerization of propylene with these supported catalysts! Polymer stereoregularity (^{13}C NMR), molecular weights (GPC) and weight distributions (GPC), and degree of crystallinity (WAXD and DSC) are virtually identical when comparing supported and soluble catalysts.

There is, of course, the obvious concern that the supported catalysts prepared are not, in fact, supported

Table IV
Propylene Polymerization with Compounds 1 and 2 Supported on Silica or Alumina and Polypropylene Properties[a]

catalyst/support	Zr (μmol)	yield (g)	R_p[b]	% mmmm[c]	T_m (°C)[d]	M_n[e]	M_w/M_n[e]	% cryst (DSC/WAXD)[f]
1/PDA–$AlMe_3$	3.0	2.5	185	89.7	143	19500	1.61	45.8/55.0
1/PDS–$AlMe_3$	2.0	6.2	689	89.0	143	19000	1.68	42.3/56.7
1/none	2.35	15.3	1450	89.9	142	18000	1.68	45.5/57.2
2/PDS–$AlMe_3$	2.0	3.0	330	91.8	139	6800	2.8	37.0/[g]
2/none	2.2	18.0	1800	90.4	136	6000	2.7	40.4/[g]

[a] Conditions: 500 mL of toluene, 5.2 mmol of Al as MAO, $p_{C_3H_6}$ = 3.0 atm, T = 30.0 ± 0.5 °C, t = 1.5 h, 1500 rpm. [b] Average rate of polymerization in kg of PP/mol of Zr × h × atm. [c] Determined from the ^{13}C NMR spectrum of unfractionated polypropylene. [d] Determined from the DSC trace of unfractionated polypropylene. [e] Determined from the DRI chromatogram and universal calibration curve. [f] Percent crystallinity as measured by DSC[18] or WAXD.[20] [g] Not determined.

Table V
Polymerization of Propylene Using Compound 1 Supported on PDS–$AlMe_3$[a]

entry	toluene (mL)	support (g)	Zr (μmol)	Al (mmol)[b]	time (h)	T (°C)	yield (g)	R_p[c]
1[d]	100	0.11	8.7	5.2	1.0	28–33	1.70	65
2[e]	119	0.00		8.7	1.0	32–37	0.036	
3[f]	86	0.00	2.4	6.2	0.5	22–41	4.60	1280
4[g]	120	0.20	15.8	0.0	1.0	30–34	0.125	2.64
5[h]	72	0.12	9.5	5.2	1.0	23–31	0.79	27.7

[a] Polymerizations were conducted in a small autoclave without temperature control or efficient stirring under pressure of C_3H_6 (3.0 atm). [b] The value quoted is based on aluminoxane only. [c] Average rate of polymerization in kg of PP/mol of Zr × h × atm. [d] Polymerization conducted using supported catalyst and MAO. [e] Toluene-soluble portion used in the preparation of the supported catalyst from entry 1. [f] Additional compound 1 added to toluene-soluble portion used in entry 2. [g] Supported catalyst from entry 1 in the absence of MAO. [h] Addition of MAO to the catalyst used in entry 4.

at all. It is possible, for example, that the MAO that is added may cause desorption of some or all of the metallocene compound from the support, leading to the production of a (lower) amount of soluble catalyst. The similarity in polymer properties would then be expected.

The following experiments were conducted to eliminate this possibility, and the results are summarized in Table V. The supported catalyst (1/PDS–$AlMe_3$) was precontacted with a MAO solution in toluene and then filtered and washed with toluene. The filtrate was used to polymerize propylene. After 1.0 h, a portion of the mixture was withdrawn and the polymer isolated (entry 2). The remainder was treated with compound 1, and after 0.5 h the mixture was quenched and the polymer isolated (entry 3). The supported catalyst, in the absence of additional aluminoxane, retains some catalytic activity (entry 4), which is partially restored on the addition of more aluminoxane (entry 5).

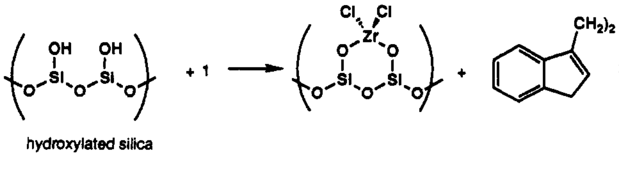
By comparing entry 1 with entry 2, it is clear that the soluble portion has a negligible amount of catalyst derived from compound 1, although MAO is clearly present in the soluble portion since high activity was restored on the addition of compound 1 (entries 2 and 3). Given the relatively low values of Al:Zr expected under the conditions of entry 4 (vide supra), the reduced activity observed is hardly surprising; it is well-known in soluble systems that catalytic activity is strongly influenced by the Al:Zr ratio employed.[2] Catalytic activity was not fully restored on addition of more MAO to the supported catalyst (entry 5); this may be due to adventitious deactivation during handling and/or irreversible deactivation of active centers on prolonged contact with MAO.[13]

Discussion

From the results summarized in Table V, it is apparent that the bulk of the polymer that is produced using these supported catalysts is derived from a heterogeneous catalyst. A negligible amount of polymer is formed by any leaching of the metallocene compound from the support. Furthermore, to obtain highest activities, an excess of MAO must be present during polymerization. We have not, as yet, addressed the issue as to whether the excess MAO can be replaced by another alkylaluminum compound without deleterious effects; this is an obvious direction for further work.[6]

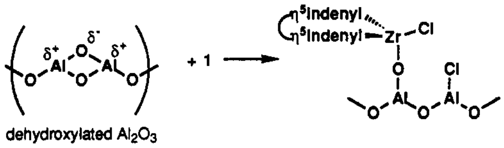
Given that the polymer properties appear to be unaffected by supporting the metallocene compound, one can conclude that most of the metallocene compound has been supported structurally intact on the trimethylaluminum-treated supports (i.e., isotactic polymer is produced and the microstructure of the polymer is very similar to that obtained under homogeneous conditions) and that the uniformity of active centers present on the surface during polymerization is much higher than that observed using a conventional heterogeneous catalyst; molecular weight distributions are narrow and comparable to those obtained using the soluble system.

As mentioned earlier, the amount of metallocene that can be adsorbed onto these surfaces is much less than one would predict based on simple, physical adsorption (Table II). The implication of this result is that the metallocene compound is adsorbed at specific sites on the surface. It is therefore, surprising that significant differences in the amounts adsorbed are not seen when comparing silica and alumina; the surface chemistry of these two supports is somewhat different following partial or "complete" dehydroxylation.[7,14]



2)

Some of the trends shown in Table III can be partially rationalized by considering the interaction of the metallocene dichloride with the support. In the case of silica, increased activity is seen as the surface is dehydroxylated. This indicates that the metallocene compound reacts with surface hydroxyl groups during adsorption to form inactive catalyst precursors and free ligand (vide supra, eq 2). A similar trend is not observed for alumina, implying that there are additional pathways for metallocene decomposition as the surface is dehydroxylated. It is possible that the high Lewis acidity of aluminum sites on dehydroxylated alumina facilitate the formation of Al–Cl bonds and Zr–O bonded species when the metallocene compound is adsorbed at these sites (e.g., eq 3). Formation of active sites from the latter species is not expected following activation with MAO.



3)

In the case of the $AlMe_3$-treated supports, the higher polymerization activities observed are consistent with little decomposition of the metallocene compound during catalyst preparation. However, in the absence of aluminoxane, these systems are not active for propylene polymerization. This indicates that the surface chemistry of the $AlMe_3$-treated supports, particularly those derived from partially dehydroxylated alumina, does not mimic that of methylaluminoxane in generating significant concentrations of active sites. This seems reasonable given that the total amount of $AlMe_3$ that is incorporated onto the support (ca. 0.85 mmol of Al/g) is similar to the amount of metallocene adsorbed (0.10 mmol/g). This corresponds to a ratio of Al:Zr of 8.5:1, which is considerably lower than that typically used in an aluminoxane-based system and may be responsible for the negligible activity seen with pretreated catalysts in the absence of MAO.

Experimental Section

All solvents, chemical reagents, and gases were purchased from commercial sources and purified as required. All reactions were conducted under an atmosphere of dry nitrogen. Toluene (BDH Omnisolve or Fisher Optima) was dried and deoxygenated by distillation under nitrogen from sodium benzophenone ketyl. Air-sensitive compounds were prepared and handled using standard Schlenk techniques.[15] Air-sensitive compounds were stored in a Vacuum Atmospheres glovebox under nitrogen. Compounds 1 and 2 and methylaluminoxane were prepared using literature procedures.[2g,16] ^{13}C NMR spectra of polypropylene were obtained using 5–15% w/w solutions in 1,2,4-trichlorobenzene at 75.43 MHz on a Bruker AC 300 spectrometer at 120 °C. Chemical shifts were referenced internally to the polypropylene mmmm CH_3 peak (21.78 ppm relative to TMS).[17] All experiments were run with inverse gated decoupling to minimize NOE and allow for quantitative results. Spectra were recorded with a pulse delay of 1.7 s with a digital resolution of 0.7 Hz/point corresponding to a data length of 32K. The pulse angle and acquisition time were 30° and 1.3 s, respectively. A sweep width of 0–160 ppm was used. Field/frequency lock was established using DMSO-d_6. Melting endotherms were recorded using differential scanning calorimetry. The polypropylene samples were annealed in aluminum pans by heating the samples at 5 °C/min from 40 to 180 °C prior to cooling at a rate of 10 °C/h in an oven purged with nitrogen. Using a Du Pont 910 DSC instrument, the melting endotherm of each sample was measured by heating the sample at 10 °C/min from 40 to 170 °C. Heats of fusion were determined using planimetry and were used to determine crystallinity (100% 39.4 cal/g).[18] Gel permeation chromatography analysis was conducted on a Waters 150C high-temperature gel permeation chromatograph using a refractive index detector at 145 °C. 1,2,4-Trichlorobenzene containing 0.1% Irganox 1010 as an antioxidant was used as the eluent. The molecular weights were determined using a universal calibration curve for polystyrene. The Mark–Houwink constants used were as follows: polypropylene, $K = 0.0142$ cm^3/g and $a = 0.67$; polystyrene, $K = 0.0121$ cm^3/g and $a = 0.707$.[19] Wide-angle X-ray diffraction measurements were made using a Siemens D500 diffraction system. The radiation source was nickel-filtered Cu Kα (40 kV and 30 mA). The samples were scanned over a 2θ range of 5–40° at a scan rate of 0.02°/s. Powder samples were annealed in a vacuum oven at 90 °C for 24 h and allowed to cool slowly prior to analysis. Diffraction data were analyzed for percent crystallinity using EVA software according to the literature.[20] Elemental analyses were determined by M.H.W. Laboratories, Phoenix, AZ.

Determination of Oxide Surface Hydroxyl Content.[8,9] A weighed sample of PDA (0.25 g, 2.45 mmol) was suspended in dry ether (10 mL) in a dry, two-neck flask connected to a gas buret. A solution of MeLi in ether (1.4 M, 0.5 mL, 0.7 mmol) was added via syringe at room temperature. The mixture was vigorously stirred, and the amount of gas evolved was measured after evolution had effectively ceased (8.63 mL after correction for the volume of ether added). The oxide surface hydroxyl content (in mol of OH/mol of support) was calculated using the ideal gas law.

A similar procedure was employed using trimethylaluminum, except that the support was slurried in toluene. The results of these analyses, which were not corrected for the solubility of methane in ether or toluene, are summarized in Table I.

Methylaluminum Content of the Supports PDA–$AlMe_3$ and PDS–$AlMe_3$. PDA–$AlMe_3$ (1.48 g, ~0.0145 mol of Al_2O_3) was slurried with toluene (20 mL) in a two-neck flask connected to a gas buret. Methanol (5 mL) in toluene (20 mL) was added with vigorous stirring, and the amount of gas evolved was measured. After evolution had ceased the temperature (294 K), pressure (733 mmHg), and volume (63.45 mL) were recorded. This volume corresponds to 0.174 mol of CH_4/mol of PDA or 0.087 mol of Al/mol of PDA.

In a similar experiment using PDS–$AlMe_3$, 1.34 g (~0.0223 mol) of SiO_2 was hydrolyzed as described above. A total of 59.7 mL of CH_4 was evolved at 747 mmHg and 297 K. This volume corresponds to 0.108 mol of CH_4/mol of PDS. This is equivalent to the surface hydroxyl content of 0.054 mol of OH/mol of support (see Table I).

Adsorption of Metallocenes on Supports. A solution containing 106 mg of compound 1 in toluene (112 mL) was added to 1.30 g of PDA in a round-bottom flask attached to a Schlenk filter and stirred under nitrogen in the dark for 24 h. The slurry was filtered under N_2, and the solid was washed with dry toluene (3 × 5 mL). The supported metallocene was then dried in vacuo.

To determine the concentration of metallocene on the support, the filtrate was diluted to volume (200 mL). An aliquot was then analyzed by UV–visible spectrophotometry at 429 nm ($\epsilon = 2554 \pm 27$ M^{-1} cm^{-1}). This method indicated that 24.9 mg of metallocene was present in the filtrate. Therefore it was determined that the catalyst loading on the PDA was 62.4 mg of compound 1/g of PDA. Elemental analysis calculated for 62.4 mg of $C_{20}H_{20}ZrCl_2$/g of PDA: C, 3.55; H, 0.29; Cl, 1.05. Found C, 3.29; H, 0.54; Cl, 1.21.

In the case of compound 2, the analysis was performed at 318 nm ($\epsilon = 2295 \pm 23$ M^{-1} cm^{-1}). The metallocene loadings on each of the supports studied were determined by UV–visible spectrophotometry, and the results are summarized in Table II.

In a separate experiment employing compound 1 and PDS or PDA, the soluble portion was concentrated in vacuo and analyzed by ^1H NMR. In addition to unreacted compound 1, the presence of bis(indenylethane) was evident.[16] The relative molar amounts of compound 1 and ligand present were determined by integration of the signals at δ 6.19 and 6.3, respectively: 4.6:1 for PDA and 1.5:1 for PDS. The amount of metallocene present was in agreement with that determined by UV–visible spectrophotometry.

When this experiment was repeated using the trimethylaluminum-treated PDS, only compound 1 was detected in the soluble filtrate. The amount of compound 1 that was present was in agreement with that determined by UV–visible spectrophotometry.

Hydrolysis of Methylaluminoxane. Methylaluminoxane (0.206 g) was suspended in toluene (20 mL) in a single-neck flask equipped with a pressure-equalizing dropping funnel connected to a gas buret. With stirring, acidic methanol (5 mL) was added, and the methane evolution was measured. After evolution had ceased the temperature (296 K), pressure (737 mmHg), and volume of gas evolved (121.5 mL) were recorded. This volume corresponds to 23.6 mmol of CH_4/g of MAO or 1.54 mol of CH_4/

mol of Al based on the molecular weight reported for methylaluminoxane.[11]

Adsorption of Methylaluminoxane on Supports; Determination of Bound Aluminoxane. Partially dehydroxylated alumina (0.097 g) was added to a 100-mL, two-neck, round-bottom flask in a glovebox along with methylaluminoxane (0.39 g) and toluene (20 mL). After stirring for 1 h at 25 °C, the mixture was filtered and the support was washed with toluene (3 × 5 mL). The filtrate was concentrated to dryness in vacuo, providing 0.31 g of MAO. Thus, a loading of 0.82 g of MAO/g of PDA or 12.5 mmol of Al/g of PDA was obtained.

Similar experiments with PDS, PDS–$AlMe_3$, and PDA–$AlMe_3$ resulted in 0.69, 0.45, and 0.58 g of MAO/g of support.

Determination of Bound Methylaluminoxane Content by Hydrolysis. A weighed amount of PDA that had been treated with methylaluminoxane (total 0.152 g, corresponding to 0.083 g of PDA; see above) was suspended in toluene (20 mL) in a single-neck flask equipped with a pressure-equalizing dropping funnel connected to a gas buret. With stirring, acidic methanol (5 mL) was added, and the gas evolution was measured. After evolution had ceased the temperature (295 K), pressure (731 mmHg), and volume of gas evolved (47.3 mL) were recorded. This volume corresponds to 12.4 mmol of CH_4/g of support or 22.6 mmol of CH_4/g of PDA. This result is close to the amount of MAO supported, as determined above (0.96 g of MAO/g of PDA vs 0.82 g of MAO/g of PDA).

Polymerization of Propylene Using Catalysts 1 and 2. Method A. Methylaluminoxane (300 mg, 5.2 mmol of Al based on $[CH_3AlO]_n$) was weighed into a glass insert in a glovebox, the insert was then placed in a 300-mL Parr autoclave equipped with a thermocouple, septum port, and stirbar, and the vessel was sealed and removed from the box.

In a separate flask, a suspension of the supported catalyst (or a solution of compound 1) in 5.0 mL of toluene was prepared under nitrogen.

Toluene (ca. 100 mL) was added to the autoclave through the septum port via syringe and the system was then pressurized with C_3H_6. After the toluene was saturated with propylene, the pressure was briefly released and the catalyst suspension (or solution) was injected by syringe against a 1.0-atm backpressure of C_3H_6. The vessel was then repressurized and stirred for 1.5 h while monitoring the temperature. The monomer was then bled off and the mixture quenched with methanol. The toluene was removed in vacuo, and the polymer was slurried in methanol, filtered, washing with methanol, and then dried in vacuo. For polymerizations where little material was produced, the polymer was agitated in a blender with 3 M (1:1 HCl:methanol) for 15 min to remove aluminoxane residues, prior to washing with methanol and drying in vacuo.

The results are summarized in Table III.

Method B. Methylaluminoxane (300 mg, 5.2 mmol of Al based on $[CH_3AlO]_n$) was dissolved in 20 mL of dry toluene in a 50-mL gas-sampling vessel equipped with two valves and Swagelok fittings. The solution was flushed into a 1-L Zipperclave reactor with 500 mL of toluene under nitrogen pressure. The reactor was saturated with propylene at a temperature of 30 ± 0.5 °C and 3.0 atm while stirring at 1500 rpm. A weighed amount of the catalyst was suspended in 5.0 mL of toluene, and the suspension (or a known amount of compound 1 or 2 dissolved in toluene) was injected via syringe under pressure. Polymerizations were stopped by venting the reactor and draining the polymer slurry through a ball valve in the reactor bottom into a small volume of methanol, under nitrogen.

The polymer was isolated as described above, and the results are summarized in Table IV.

Method C (Table V, Entry 1). The procedure described under method A was followed using 0.11 g of PDS–$AlMe_3$ on which was supported 33.5 mg of compound 1/g of support. After 1.0 h, 1.7 g of polymer was isolated.

Method D (Table V, Entries 2 and 3). The support used in method C (0.2 g) was stirred with a solution of methylaluminoxane (0.6 g, 10.4 mmol) in 142 mL of toluene. The suspension was filtered in the glovebox through a 4–5.5-μm frit, and 119.0 mL of the filtrate was placed in the Parr autoclave. The insoluble portion was washed with toluene (10 mL) and dried in vacuo (0.25 g).

The autoclave was pressurized with C_3H_6 (3.0 atm) while stirring for 1.0 h. The reactor was vented and 33.0 mL of the suspension was withdrawn by syringe. The polymer was isolated as described above and 0.01 g of polypropylene was obtained (corresponding to a total of 0.036 g of polymer).

To the remaining solution (86.0 mL) was added a solution of compound 1 in toluene (1.0 mg in 5.0 mL) under propylene pressure (3.0 atm). After 30 min, the vessel was vented and the mixture quenched with methanol. A total of 4.6 g of polymer was isolated.

Method E (Table V, Entries 4 and 5). The insoluble portion from method D was suspended in 120 mL of toluene in the autoclave and the system pressurized with propylene. After 1.0 h, 48.0 mL of the mixture was removed and 0.05 g of polypropylene was obtained (corresponding to a total of 0.125 g of polymer). To the remaining mixture was added 0.3 g of MAO in toluene (5.0 mL). After 1.0 h, the mixture was vented and quenched with methanol. A total of 0.86 g of polypropylene was isolated as described above (corresponding to an additional amount of polymer = 0.79 g).

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References and Notes

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