

Ethylene polymerization using silica-supported zirconocene dibromide/methylalumoxane catalysts

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Abstract

Functionalized metallocene precursors $(\text{BrMe}_2\text{SiC}_5\text{H}_4)\text{CpZrBr}_2$ (**1**), $(\text{BrMe}_2\text{SiC}_5\text{H}_4)_2\text{ZrBr}_2$ (**2**), $(\text{Br}_2\text{MeSiC}_5\text{H}_4)_2\text{ZrBr}_2$ (**3**), and $[\text{1,3}-(\text{BrMe}_2\text{Si})_2\text{C}_5\text{H}_3]_2\text{ZrBr}_2$ (**4**) were immobilized on partially dehydroxylated silica (PDS) and screened for ethylene polymerization in slurry reactions conducted in toluene using methylalumoxane (MAO) as the cocatalyst. The effects of metallocene precursor structure, catalyst immobilization method, and catalyst loading are presented in terms of catalytic activity, polymer molecular weight distribution, and stability of the catalysts toward leaching.

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1. Introduction

Upon activation with methylalumoxane (MAO), group 4 metallocene complexes are active catalysts for homogeneous polymerization of ethylene and α -olefins. The advantages of metallocenes compared to conventional Ziegler-Natta catalysts are well known, and foremost among these is the ability to tailor the structure of the complex to individual process requirements. Gas-phase polymerization methods commonly used in commercial applications require that the metallocene be supported on a dispersant such as silica. Common problems in immobilization methodology include synthesis of suitably functionalized metallocene precursors, characterization of the supported metallocene, and catalyst stability under polymerization reaction conditions. Ultimately one hopes to maintain, upon immobilization, the high activity of the metallocene as well as its characteristic single-site behavior as reflected in the polymer molecular weight distribution and microstructure [1–3].

Metallocenes readily adsorb onto oxides such as silica [4–6], and “directly deposited” metallocene catalysts can be surprisingly effective [7]. An arguably more general approach initially treats the adsorbant with the

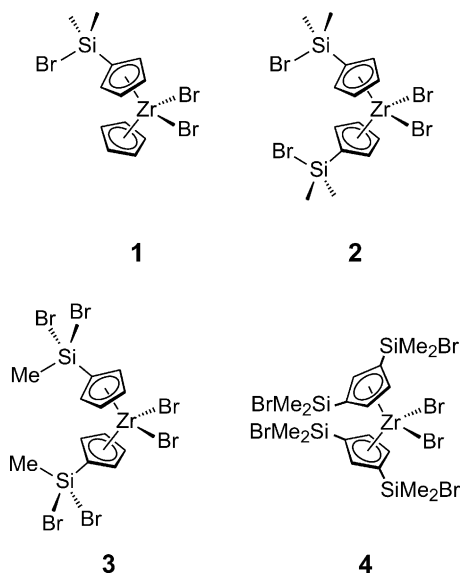
cocatalytic material, usually an alkylaluminum compound, before adding the metallocene to form a hybrid catalyst. Catalyst–cocatalyst interactions (probably ion-pairing) hold the system together during the ensuing polymerization reaction [8–20]. In a third approach, the metallocene is covalently tethered to the silica surface by means of rational synthesis. Several interesting reports of covalently tethered metallocene catalysts have demonstrated the viability of this approach [21–28]. The obvious disadvantage here is the extra synthetic burden, but the potential benefit is an improved, fundamental understanding of structure–property relationships arising from the metallocene–support interface.

We reported a convenient, highly general synthesis of group 4 metallocene dibromides bearing BrMe_2Si and Br_2MeSi substituents [29,30]. Because the Si–X bonds are significantly more reactive than corresponding M–X bonds toward nucleophiles such as water [29,31–37], we envisioned the use of these electrophile-functionalized complexes as precursors to supported metallocene olefin polymerization catalysts. Others have shown that metallocene dichlorides (or ligand precursors) bearing pendant SiX groups at the terminae of polymethylene or related “spacers” react preferentially with hydroxyl (silanol) groups on silica [22,24,25,38–40]. Our synthetic method offered the possibility of varying the number and regiochemistry of relatively short tethering groups (as in complexes **1–4**) as a means of exploring the role of the metallocene–silica

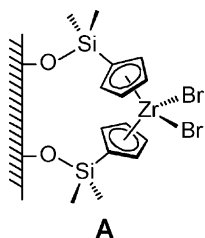
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interface in determining polymerization outcomes. Our specific aim was to identify particular metallocene precursors that would react with hydroxyl (silanol) groups on the



surface of partially dehydroxylated silica (PDS) to give a supported metallocene in which the reactive MX_2 portion of the complex is held in a “face-up” configuration (A). This report describes our effort to develop such a catalyst for ethylene polymerization [41]. Although we largely failed to demonstrate the “face-up” geometry conclusively using various spectroscopic tools, the empirical polymerization results nevertheless provide correlations among precursor structure, immobilization methods, and catalytic activity that we interpret in terms of such canonical models.



2. Experimental

2.1. General procedures

All reactions were carried out using standard inert-atmosphere techniques. Solution NMR spectra were recorded on a JEOL Eclipse-500 instrument. CPMAS ^{13}C NMR spectra were recorded on a Bruker MSL-300 instrument. CPMAS NMR samples were packed into rotors in a nitrogen glove box and maintained under a nitrogen atmosphere during data collection. GPC analyses were conducted at Dow Chemical Company (Midland, MI) using a Waters 150C instrument equipped with a refractive index detector and calibrated

with polystyrene standards. The chromatographic eluent was trichlorobenzene (130°C). Elemental (combustion and ICP) analyses were performed by Desert Analytics (Tuscon, AZ). X-ray photoelectron spectra (XPS) were obtained using a PHI 5400 instrument. XPS samples were mounted as powders on two-sided adhesive tape. Solvents were purified according to published methods [42]. Me_3Al “depleted” MAO was prepared by evaporating a 30% toluene solution (Albemarle) under high vacuum (2×10^{-3} Pa) and washing the resulting glassy, colorless solid with hexane. Triethylamine was freshly distilled from CaH_2 . $^{13}\text{CH}_3\text{Li}$ (lithium iodide complex) was prepared from $^{13}\text{CH}_3\text{I}$ and lithium metal in diethyl ether. The resulting ethereal organolithium solution was filtered, evaporated to dryness, and stored in a nitrogen glove box. Complexes 1–6 were prepared as described elsewhere [29,30].

2.2. Silica preparation

Our sample of Grace 948 silica had an average particle size of $56\ \mu\text{m}$, a pore volume of $1.6\ \text{ml g}^{-1}$, and a surface area of $300\ \text{m}^2\ \text{g}^{-1}$, typical characteristics for this silica grade. A portion of silica was gently packed into a clean quartz tube, which was plugged with quartz wool at both ends. The tube was fitted into a tube furnace and then cautiously evacuated by interfacing to a high vacuum line. The tube was heated at a rate of $20^\circ\text{C min}^{-1}$ to 500°C . After 6 h at 500°C , the tube had reached an ultimate vacuum of 1×10^{-3} Pa. After cooling overnight under continued vacuum, the tube containing the partially dehydroxylated silica was transferred to a nitrogen glove box.

2.3. General metallocene immobilization procedure

In the glove box, 200–400 mg of PDS and a functionalized metallocene compound (10–40 mg) were transferred to a swivel-frit apparatus. After interfacing the fritte to a vacuum line, about 20 ml of dichloromethane was vacuum-transferred from P_2O_5 onto the silica at -78°C . In the “excess amine” preparations, 2 ml of triethylamine was then injected under an argon counterstream, and the mixture was stirred for 1 h under argon at 25°C and then filtered. In the “no amine” preparations, no amine was added, and the silica slurry was stirred under reflux for 15 h and then filtered. In either preparation, the filtrate was evaporated, leaving a residue. The silica collected on the filter was washed with CH_2Cl_2 ($3 \times 10\ \text{ml}$), dried under vacuum at 25°C for 15 h, and transferred to a nitrogen glove box. The filtrate residue was analyzed by ^1H NMR spectroscopy. In the “excess amine” preparations, HNET_3Br was identified by its characteristic spectrum in CDCl_3 : δ 11.2 (br s, 1 H, NH), 3.12 (m, 6 H, CH_2), 1.44 (t, 9 H, CH_3). Metallocene byproduct species were tentatively assigned in the residues of the “no amine” preparations as described in the text.

2.4. Slurry polymerizations

The reactor was a 1.5-l flanged Pyrex kettle equipped with a thermocouple, an ethylene inlet, a septum-sealed injection port, and a teflon-sealed overhead paddle stirrer fitted through a condenser. After drying in an oven for several hours, the reactor components were transferred to a nitrogen glove box while still warm. The reactor was assembled in the glove box, and a measured amount of an immobilized zirconocene catalyst and an excess of MAO (nominally Al:Zr = 5000) were loaded into the reactor. An arbitrarily high Al:Zr ratio was chosen to ensure complete scavenging of the large solvent volume. Outside the glove box, 400 ml of toluene pretreated with 50 mg of MAO at 50 °C was transferred into the reactor under nitrogen. The mixture was stirred for 10 min while equilibrating the reactor temperature to 50 °C using an agitated water bath interfaced to an Omega thermostat. Then, ethylene (purified by passage over Engelhard Q5 oxygen scavenger and Davison 10X molecular sieves) was admitted through an immersed gas dispersion tube to initiate polymerization. Excess ethylene was to a mineral oil bubbler. Temperature was maintained at 50(2) °C. After reacting for 10 min, 20 ml of acidified methanol (prepared by diluting 50 ml of concentrated hydrochloric acid to 1 l with methanol) was added to quench the reaction. The reactor was vented, and the contents were poured into 200 ml of rapidly stirred acidified methanol. The polymer was collected on a filter, washed with methanol, and dried in a vacuum oven at 75 °C for at least 12 h. In some preliminary experiments, the kettle was pre-saturated with ethylene and the solid catalyst was placed in a glass loop and blown into the reactor in a nitrogen stream to initiate polymerization, but this method gave much lower activities, probably because the immobilized catalyst needed time for solvent wetting and catalyst activation.

2.5. Leaching experiments

The reactor was assembled as above, but the catalyst and MAO were excluded. Instead, the reactor was charged with toluene (350 ml) and a small amount (50 mg) of MAO as a scavenger and then equilibrated at 50 °C. Meanwhile, a slurry of the immobilized catalyst (200–400 mg), toluene (100 ml), and MAO (5000 eq.) was added to the flask, and the resulting mixture was stirred at 50 °C for 10 min. Half of this mixture was then transferred to a fritted glass filter mounted on one of the kettle inlets, and an overpressure of nitrogen was used to force the supernatant through the reactor. The filtration generally took about 20 min. After the filtration was complete, ethylene was introduced into the reactor and the remainder of the experiment was conducted in the same manner as the slurry polymerizations.

3. Results and discussion

3.1. Support preparation

Much discussion has appeared in the literature about how best to treat the silica prior to immobilizing the metallocene. We rejected chemical methods designed to isolate hydroxyl groups from one another, such as pretreatment with trialkylsilyl chlorides [43,44], or calcination at temperatures exceeding 600 °C. Compounds **2–4** require adjacent hydroxyl groups to anchor all of the SiMe₂ groups to the silica surface. For example, in the crystal structure of **3**, the Si–Si distance is 760 pm [30]. The compound is fluxional in solution, and the Si–Si distance may change in order to adapt to the surface hydroxyl spacing. However, we reasoned that a nominal surface hydroxyl density of 2–3 OH groups/nm² would be ample. We therefore simply dehydroxylated our silica at 500 °C under vacuum (2×10^{-3} Pa), conditions which have been shown to afford approximately the desired hydroxyl density [45–48].

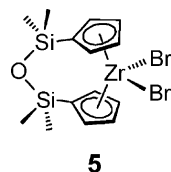
3.2. Precursor synthesis

Complexes **1**, **2**, and **4** were prepared by treating the corresponding trimethylsilyl-substituted metallocene dichlorides with excess boron tribromide in 1,2-dichloroethane at 80 °C following our published procedures [29,30,41]. Similarly, complex **3** was prepared by treating the corresponding bis(methyldiphenylsilyl)-substituted metallocene with excess BBr₃ [30]. These reactions afford crystalline products in high yield and purity. These complexes were chosen to vary the number of potential surface tethering groups. Although complex **3** probably cannot utilize all of its Si–Br functional groups when grafting to a silica surface having only 2–3 OH groups/nm², we reasoned that **3** might have a greater propensity than **2** to utilize two anchoring points.

3.3. Immobilization studies

We developed two methods of immobilizing our metallocene catalysts on partially dehydroxylated silica. In the first (“no amine”) method, samples of silica were treated with a metallocene precursor (**1–4**) in refluxing dichloromethane. The use of a higher-boiling solvent (1,2-dichloroethane, bp 80 °C) resulted in decomposition. In the second (“excess amine”) method, the metallocene precursor and PDS were treated with triethylamine (to remove the HBr byproduct) in dichloromethane under mild conditions (typically 25 °C, 1 h). Our primary means of determining the success of immobilization was to analyze, using ¹H NMR spectroscopy, the residues obtained after washing the metallocene-treated silica samples with dichloromethane. In the “excess amine” method, the NEt₃HBr byproduct dominated the spectrum, but importantly, no signals from metallocene compounds were ever observed. We concluded that all of the added metallocene had been grafted onto the

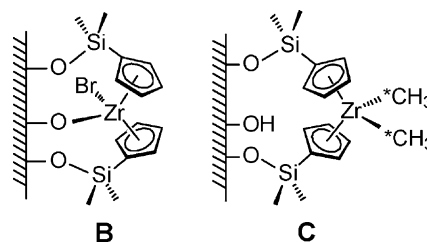
silica. In the “no amine” method, a pale yellow residue was obtained which, when dissolved in CDCl_3 , showed several weak multiplets in the Cp region of the ^1H NMR spectrum and a dense cluster of signals centered at 0.44 ppm in the SiMe region, which we assigned to unreacted metallocene and hydrolysis products thereof. In preliminary studies using samples of silica dehydrated at temperatures lower than 500°C or under helium flow instead of high vacuum, residues contained mainly the disiloxane-bridged hydrolysis product (**5**).



3.4. Supported catalyst characterization

The amount of metallocene present in the residue from the “no amine” immobilization procedure could not be weighed accurately, so the assay of zirconium in the supported catalysts were determined instead by sodium carbonate fusion followed by ICP analysis. X-ray photoelectron spectroscopic analyses were carried out on several samples of supported metallocenes, and invariably these spectra showed Zr:Br mole ratios ranging from 1:1 to 1.5:1. Because the ZrBr_2 group of the metallocene is relatively stable toward water under neutral or acidic conditions, we believe exposure of the samples during transfer to the spectrometer antechamber should not have hydrolyzed the ZrBr_2 groups to ZrBr(OH) groups, however, any remaining Si–Br groups probably were hydrolyzed. The resolution of the XPS experiment is not adequate to discriminate Br and OH ligands by analyzing the lineshape of the Zr (3d) signal alone [49]. The only remaining plausible explanation is that the catalyst has adopted one of many possible “face-down” configurations (e.g., **B**). The putative supported metallocene **B** was prepared using **2** as the precursor and then treated with excess $^{13}\text{CH}_3\text{Li}$. The CPMAS ^{13}C NMR spectrum (Fig. 1) shows the appearance of a signal at about 20–30 ppm, which we assign to a Zr– CH_3 group (**C**) [5,50], although the resolution

is not adequate to determine if **C** has a ZrMe_2 group or a Zr(Br)Me group or a Zr(O)Me group or a mixture of these. This result shows that even if the catalyst initially adopts a “face-down” configuration as in the canonical structure **B**, the general metallocene structure is still retained and still engages in elementary chemical reactions such as substitution of methyl for bromide. Unfortunately, because the catalyst was so dilute (1%) in the silica support, we were unable to obtain meaningful transmission or reflectance infrared spectra to obtain more conclusive information about the metallocene–silica interface.



3.5. Ethylene polymerization studies

Table 1 presents our polymerization data. All polymerizations were carried out at $50(2)^\circ\text{C}$ in toluene under 1 atm of ethylene pressure and using 5000 nominal eq. of MAO cocatalyst to ensure thorough scavenging of the solvent. We explored the effects of precatalyst structure (**1–4**), the effects of different methods of preparing the supported catalysts (“no amine” or “excess amine”), and the effect of catalyst loading on productivity and catalyst stability (leaching).

Entries 1–4 compare the four catalysts **1–4**, respectively. All four were immobilized on silica using excess triethylamine base, and all catalyst loadings and polymerization reaction conditions were the same. The activity of the catalyst decreases as the number of tethering points increases. Either the catalyst becomes irreversibly locked in a “face-down” configuration (**B**), or the additional tethers simply restrict the conformational freedom of the catalyst on the surface, preventing monomer uptake. However, some of this activity trend is probably due to increasing catalyst stability as reflected in the leaching data (Table 1, entries 1–4, at right). Starting with either **1**, **2**, or **3** as the catalyst precursor, leached (homogeneous) species probably most closely resemble the disilylated model complex **6** or, if there is any hydrolysis, the bridged complex **5** (M:Zr). The latter are highly active catalysts in solution as shown by control experiments (entries 8 and 9). (The slightly elevated PDI values for entries 8 and 9 relative to the typical value of 2.0 for homogeneous metallocene-catalyzed polymerizations arise from introducing the ethylene to initiate polymerization rather than injecting catalyst into a pre-saturated ethylene solution.) To compare activities directly, both the supported catalyst and the leachate were presumed to have the same nominal zirconium concentration as the as-prepared supported catalyst (but see below). Thus lower activity in the leaching experiments

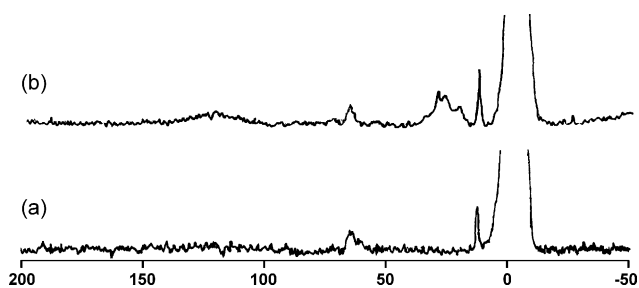


Fig. 1. CPMAS ^{13}C NMR spectra of (a) partially dehydroxylated silica + $^{13}\text{CH}_3\text{Li}$; (b) catalyst [2] supported on PDS and treated with $^{13}\text{CH}_3\text{Li}$.

Table 1
Ethylene polymerization data^a

Entry	Catalyst	Silica-supported catalyst data						Leach filtrate data			
		Preparation	Loading ^b	Productivity ^c	M_n	M_w	PDI	Productivity ^c	M_n	M_w	PDI
1	1	— ^d	1.1	5.8(4)	1.7	8.7	5.1	8.2	3.6	8.7	2.2
2	2	— ^d	1.1	1.3(1)	1.3	8.4	6.7	1.5	2.2	8.6	3.8
3	3	— ^d	1.1	0.60(6)	1.7	9.0	5.3	0.6	3.6	9.5	2.7
4	4	— ^d	1.1	0.31(1)	1.1	7.8	7.1	0.05	1.0	3.3	3.2
5	3	— ^e	1.1	1.0(2)	0.6	9.8	16.0				
6	3	— ^f	0.4	2.4(1)	1.5	8.6	5.81	2.5	4.7	11.6	2.45
7	3	— ^d	0.3	1.1(7)	1.1	7.9	7.3	1.9	2.2	8.6	3.9
8	5	— ^g		70(5)	4.1	10.2	2.5				
9	6	— ^g		93(7)	4.1	11.0	2.7				

^a Polymerizations carried out in 400 ml of toluene using MAO cocatalyst (nominal Al:Zr = 5000:1) at 50 °C under 1 atm of ethylene for 10 min.

^b Catalyst loading expressed as mol% of Zr in silica.

^c Total productivity expressed in Mg mol⁻¹ h⁻¹. Relative errors in parentheses are standard deviations for three experiments. Leach filtrate productivities assume the same [Zr] as the as-prepared silica-supported catalysts.

^d Supported on silica using excess NEt₃ base.

^e Supported on silica using 1 eq. of NEt₃ base.

^f Supported on silica without NEt₃ base.

^g Homogeneous catalyst.

(entries 1–3) clearly suggests a trend toward increasing catalyst stability. In the case of **3** one could conclude alternatively that the likelihood of forming two grafts using **3** is higher than when using **2**, and that the result obtained using **2** is therefore intermediate between a singly and doubly-tethered catalyst. In the case of **4**, one could pose an alternative explanation that increased steric effects of the four silyl substituents simply impede monomer enchainment. Comparing entries 3 and 6, we find that the use of triethylamine base during catalyst immobilization results in a catalyst that is both less active and more stable toward leaching. Comparing entries 3 and 7, we find that a lower catalyst loading increases apparent catalyst productivity at the expense of stability. Perhaps the catalyst first selects exposed, reactive surface sites, whereas the additional catalyst is immobilized in more secluded areas of the silica pore structure. Binuclear interactions at either loading are possible but unlikely.

At first glance, the activity data in Table 1 suggest that all of the polymerization activity of the supported catalysts arises from leached (homogeneous) catalyst. However, it is important to note that in the leaching experiments, the catalyst was exposed to MAO solution for nearly twice as long as in the slurry polymerization experiments because of the rather lengthy interval required to complete the filtration. This experimental detail explains why, for example in entries 1, 2, 6, and 7, the leach filtrate actually showed *higher* activity than the supported catalyst. However, the broad molecular weight distributions for the supported catalyst and the apparent bimodality in many of the GPC traces suggests that the supported and leached catalysts give roughly equal overall productivities over the shorter slurry polymerization intervals, whereas the supported metallocene affords a polymer with lower M_n . Proton NMR analysis shows that

the polymers obtained from the supported catalysts are free of branching, so the supported catalyst itself is not ill-behaved. However, because the *native* productivity of the leached (homogeneous) catalyst is about 100 times that of the supported catalyst, it appears that only about 1% of the metallocene is leached during polymerization. We attempted to analyze the leachate for zirconium but the amount of zirconium was apparently below the detection limit of the method. Nevertheless, the amount of metallocene leached is generally consistent with analogous supported metallocene catalyst systems reported elsewhere [24,51–55].

4. Conclusions

Electrophile-functionalized metallocene complexes serve as precursors to silica-supported metallocene ethylene polymerization catalysts. While the activity and molecular weight data are not immediately promising, we believe that additional tuning of the immobilization conditions and control over catalyst leaching could lead to a useful catalytic system. Work is underway to incorporate catalysts **1–4** in a sol–gel network to address the leaching issue, and preliminary experiments in our laboratory show that both catalytic activity and stability are markedly improved.

Acknowledgements

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