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Supported Ionic Metallocene Polymerization Catalysts

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Introduction. Metallocene-based olefin polymerization catalysts, especially those using methylalumoxane as a cocatalyst, have been the focus of intense study in recent years.[1] Academic investigators have gained insights into fundamental chain-growth processes by exploiting the chemical simplicity of these systems and the ease with which they can be rationally modified. In the industrial sphere, the high activities of these catalysts and the improved properties imparted by the structurally homogeneous polymers they produce have aroused considerable interest by polyolefins producers.

Regardless of the chemical elegance of single-site catalysts or the market potential of the resins they make, these systems would be doomed to a marginal commercial existence if they could not be made to function effectively in various polymerization processes. Soluble metallocene catalyst systems have been used successfully in low- or high-pressure solution processes to produce low-crystallinity, very low-density ethylene copolymers and elastomers. On the other hand, continuous slurry, fluidized-bed gas-phase, or bulk-monomer processes are used to produce more crystalline linear-low-density ethylene copolymers, high-density polyethylene, or stereoregular polypropylene. Since these polymers are insoluble in the reaction media, these processes require a morphologically uniform polymer product in order to avoid reactor fouling. This in turn suggests immobilizing the metallocene catalyst on a suitable support. Carriers for metallocene−alumoxane catalysts have included starches,[2] clays,[3] metals and ceramics,[4] metal halides,[5] and polymers.[6] The most commonly used supports have been porous inorganic oxides, especially silica.[7]

Ionic catalysts generated by the reaction of Cp'_2MR_2 with $[HNMe_2Ph][B(C_6F_5)_4]$[8] or $[Ph_3C][B(C_6F_5)_4]$[9] are highly active for the polymerization and copolymerization of ethylene and higher α-olefins in solution. However, heterogenizing these aluminum−alkyl-free catalysts is more problematic than the alumoxane-based systems. Coordination of Lewis-basic surface oxides to the electrophilic metal center (Figure 1a) or reaction of the ionic complex with residual surface hydroxyl groups (Figure 1b) could be anticipated to diminish or extinguish catalyst activity. We have found that pretreatment of the support with a scavenger, typically a trialkylaluminum, serves to passivate the support and compatibilize it with the ionic metallocene complex. This paper outlines our successful preparation of highly active supported ionic metallocene catalysts for olefin polymerization.[10]

Results and Discussion. Davison 952 silica, heated to 800 °C to remove adsorbed moisture, is treated with a solution of 25 wt % $AlEt_3$ in heptane (3 mL/g), filtered, washed with pentane, and dried to afford a support containing about 2 wt % Al (by ICPES). The ionic catalyst can be supported by adding this treated silica to a stoichiometric mixture of dimethylmetallocene and $[Ct][B(C_6F_5)_4]$ ($Ct^+ = NMe_2Ph^+$ (**A**) or Ph_3C^+ (**B**)) in toluene and evaporating in vacuo. However, we have found it preferable to support the activator and react with the metallocene in separate steps. In the latter procedure, the activator is dissolved in CH_2Cl_2 or warm toluene, the treated support added to the solution, and the solvent evaporated in vacuo. Analysis of the supported activator by low-voltage scanning electron microscopy (LVSEM) to the 50 Å level reveals that no crystallites of the activator are formed on the silica surface, suggesting that the activator is evenly dispersed. Slurrying the supported activator in pentane and adding to it a pentane solution of a stoichiometric quantity of dimethylmetallocene generates an active catalyst. This can be used as a slurry or isolated as a free-flowing solid.

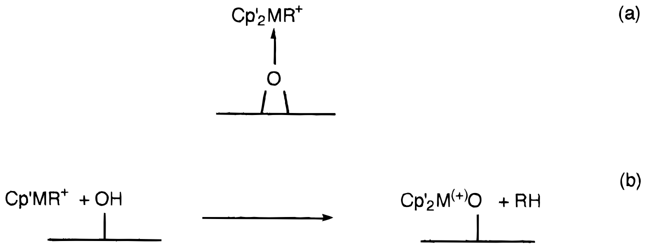

Figure 1.

Table 1. Preparation of Supported Cp_2HfMe_2 Catalysts[a]

catalyst	support	activator[b] (mg)	wt % Al	wt % Hf
1	silica	**A** (160)	2.28	0.72
2	silica	**B** (184)	2.22	0.68
3	silica	none	2.24	0.53
4	silica[c]	**A** (160)	0.06	0.70
5	cross-linked polystyrene	**A** (160)	0.92	0.70

[a] 5.00 g of support material and 80 mg Cp_2HfMe_2. [b] **A** = $[HNMe_2Ph][B(C_6F_5)_4]$, **B** = $[Ph_3C][B(C_6F_5)_4]$. [c] Not treated with $AlEt_3$.

Table 2: Ethylene Polymerization with Supported Cp_2HfMe_2 Catalysts[a]

catalyst	yield (g)	activity[b]
1	39.6	577
2	63.9	987
3	0.4	5
4	4.4	55
5	35.6	443

[a] Polymerization conditions: 250 mg of catalyst, 400 mL of hexane, 0.3 mL of 25 wt % $AlEt_3$, 13.6 atm of ethylene, 30 min run. [b] g of PE/mmol of Hf·h·atm.

The silica-supported Cp_2HfMe_2-based ionic catalysts **1**−**4** (Table 1) were used to polymerize ethylene in hexane slurry (Table 2). In all polymerizations, a small amount of $AlEt_3$ was added to the reaction medium prior to introducing the catalyst in order to remove trace reactive impurities.[11] Both $[HNMe_2Ph][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ serve to generate highly active catalysts. It is also clear from the low polymer yield from **4** that pretreatment of the support is crucial to obtaining meaningful activity. Methylalumoxane generated from the reaction of $AlMe_3$ with silica containing adsorbed water has been used as cocatalyst for metallocenes in olefin polymerization,[12] but catalyst **3** indicates that the $AlEt_3$-treated support itself is not a cocatalyst for activation of Cp_2HfMe_2. Other carrier materials can be

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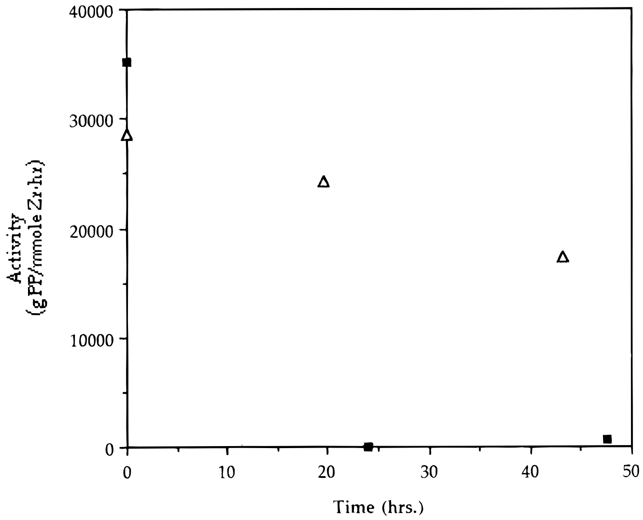

Figure 2. Activity of homogeneous and supported $Me_2Si(C_9H_{10})_2ZrMe_2-[HNMe_2Ph][B(C_6F_5)_4]$ catalysts over time. Homogeneous catalyst (■): 2 mg of $Me_2Si(C_9H_{10})_2ZrMe_2$ and 4 mg of $[HNMe_2Ph][B(C_6F_5)_4]$ in toluene (2 mL). Heterogeneous catalyst (△): 1.2 mg of $Me_2Si(C_9H_{10})_2ZrMe_2$ and 2.4 mg of $[HNMe_2Ph][B(C_6F_5)_4]$ on $AlEt_3$-treated silica (60 mg). Polymerization conditions: 400 mL of propylene, 0.3 mmol of $AlEt_3$, 60 °C polymerization temperature.

used successfully: the $Cp_2HfMe_2-[HNMe_2Ph][B(C_6F_5)_4]$ catalyst immobilized on cross-linked polystyrene (Chromasorb 101, dried at 90 °C in vacuo and treated with $AlEt_3$; catalyst **5**), polymerizes ethylene with activities similar to those of the silica-supported analogues.

Liquid α-olefins provide a suitable polymerizing medium for silica-supported chiral, stereorigid metallocenes activated by $[Ph_3C][B(C_6F_5)_4]$ or $[HNMe_2Ph][B(C_6F_5)_4]$. In bulk propylene, a $Me_2Si(C_9H_{10})_2ZrMe_2-[HNMe_2Ph][B(C_6F_5)_4]$ catalyst on $AlEt_3$-treated silica (0.8 wt % metallocene) affords isotactic polypropylene with catalyst activities as high as 80 kg PP/mmol Zr·h.[13] When the perfluorotetraphenyl borate anion is replaced by $[(C_2B_9H_{11})_2Co]^-$, however, there is no detectable activity. This is a reflection of the greater coordinating strength of the metallacarborane anion vis à vis the $[B(C_6F_5)_4]^-$ anion.[14]

Fluidized-bed gas-phase polymerization reactors rely heavily on supported catalysts. The supported ionic metallocene catalysts have been successfully used in this process. A $Me_2Si(C_9H_6)_2HfMe_2-[HNMe_2Ph][B(C_6F_5)_4]$ catalyst on $AlEt_3$-treated silica (2.5 wt % metallocene) was used in a gas-phase reactor to polymerize propylene to a morphologically uniform polymer product with a catalyst productivity of 440 g of polymer/g of supported catalyst.[15]

Another striking feature of these supported ionic metallocene catalysts is their improved lifetimes with respect to their homogeneous counterparts. Whereas fresh preparations of $Cp'_2MMe_2-[HNMe_2Ph][B(C_6F_5)_4]$ in toluene rapidly polymerize α-olefins, virtually all activity is lost if the solutions are allowed to age for 24–48 h, probably due to contact with adventitious impurities in the solvent. In contrast, silica-supported ionic metallocene catalysts lose relatively little activity over prolonged periods (Figure 2).

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Supporting Information Available: Descriptions of the procedure for preparing the supported catalyst and descriptions of the procedures for ethylene (slurry) and propylene (liquid monomer) polymerizations (2 pages). Ordering information is given on any current masthead page.

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(13) $Me_2Si(C_9H_{10})ZrMe_2$ (2 mg) and $[HNMe_2Ph][B(C_6F_5)_4]$ (8 mg) on $AlEt_3$-treated silica (250 mg) were polymerized for 15 min at 60 °C in 400 mL of propylene with 0.2 mmol of $AlEt_3$ scavenger. The yield of i-PP was 95.7 g, MW = 11 500, MWD = 2.84, mp = 138.2 °C.

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(15) Polymerizations were conducted at 65 °C using a 4 in. diameter continuous-operation fluidized-bed reactor. The gas stream consisted of 40% propylene in nitrogen at a pressure of 300 psi. Granuar polyethylene (600 g) was used as a fluid bed. Supported catalyst (70 mg) was injected every 9 min. After three bed turnovers (1800 g of collected product), the polymer product was analyzed: Mw = 117 000, MWD = 2.00, mp (by DSC) = 121.5 °C, isotacticity (%*m* by ^{13}C NMR) = 91.1%. Productivity was calculated from X-ray fluorescence analysis of residual Si in the polymer.

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