

Metallocene-Catalyzed Olefin Polymerization using Magnesium Chloride-Supported Borate Activators

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ABSTRACT: New approaches have been identified for the immobilization, on a MgCl_2 -based support, of borate activators for metallocene-catalyzed olefin polymerization. Immobilization of $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$ was carried out by reaction with a support of type $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ obtained by reaction of AlEt_3 with an adduct of magnesium chloride and ethanol. Use of the resulting immobilized borate in combination with zirconocene catalysts in ethylene and propylene polymerization resulted in significantly higher polymerization activities than were obtained using the same borate immobilized on a silica support. The MgCl_2 -

based support also gave the better polymer particle morphology, cross-sectional imaging indicating uniform support fragmentation, as opposed to incomplete fragmentation using the silica support. High catalyst activities were obtained using a $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ support impregnated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. In this case, a highly porous polyethylene particle morphology was obtained. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 986–993, 2006

Key words: polyethylene; borate activators; catalyst immobilization; magnesium chloride; metallocene catalysts

INTRODUCTION

Currently, considerable efforts are being made to develop effective techniques for the immobilization of metallocene and other single-site olefin polymerization catalysts on solid supports, a prerequisite for widespread application of such catalysts in polyolefins production.^{1–5} The most commonly used support material is silica, but the use of magnesium chloride-based supports is receiving increased attention. Recently, we and others have investigated the use of supports having composition $\text{MgCl}_2/\text{AlR}_n(\text{OR}')_{3-n}$ obtained either by the reaction of AlR_3 with $\text{MgCl}_2/\text{EtOH}$ adducts having spherical particle morphology^{6–10} or with a hydrocarbon solution of a $\text{MgCl}_2/2$ -ethylhexanol adduct, leading to in situ precipitation of the support.^{11–14}

In our initial studies, making use of spherical supports of composition $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ obtained by reaction of AlR_3 with partially dealcoholated adducts of magnesium chloride and ethanol,¹⁵ it was found that effective immobilization and activation of a range of titanium-based catalysts could be achieved via direct reaction between the support and the catalyst, without the use of methylaluminoxane (MAO) or a borate activator in polymerization.^{6,7} However, this

approach was less effective with zirconocene catalysts, which gave significantly lower ethylene polymerization activities than those obtained with the Ti-based systems.

With the aim of further extending the scope for the use of $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$ supports in the immobilization of single-site polymerization catalysts, we have now investigated the incorporation of borate activators into the support. The effectiveness of perfluoroarylboranes and borates as activators for metallocene and related metal alkyls is well established and has recently been reviewed by Chen and Marks.¹⁶ Zirconocene dialkyls are typically activated using $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ¹⁷ or $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$.¹⁸ Borate activators can also be used in combination with metallocene dichlorides, if a third component such as triisobutylaluminum able to alkylate the metallocene is present.^{19,20} Tethering of a borate activator to magnesium chloride, involving activators containing a Lewis base functionality able to coordinate to the Lewis acidic support, has recently been described.²¹ A chemically activated MgCl_2 support was treated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{NMe}_2)]$ to give an immobilized borate that was used in ethylene and propylene homopolymerization and in ethylene/1-butene copolymerization in combination with *rac*- $[\text{Me}_2\text{Si}(\text{Ind})_2\text{-ZrCl}_2]\text{Ali-Bu}_3$.

We report here on two different approaches for the incorporation of borate activators into a magnesium chloride support. In the first approach, a $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support was contacted with triethylammonium tris(pentafluorophenyl)(4-hydroxyphenyl)

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borate, $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$. This borate has previously been used in combination with silica supports pretreated with MAO or AlR_3 , with the aim of tethering the borate to the support material via reaction of a Si-O-Al-R moiety with the active hydrogen of the borate.²² The use of analogous trialkylammonium borates having long hydrocarbyl chains on the ammonium cation and having improved solubility in toluene has also been described.^{23,24} The silica-supported borates were used together with Constrained Geometry catalysts in ethylene homo- or copolymerization. Our motivation in using a 4-hydroxyphenyl borate in combination with a $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support was the possibility of immobilizing the borate via reaction with an aluminum alkyl, which is itself immobilized on magnesium chloride via the formation of coordinatively-bridged species of type $\text{Mg-O}(\text{Et})\text{-Al}$.

In a second approach, we have investigated the immobilization of a borate activator on a magnesium chloride support not by chemical bonding, but by physical impregnation. Impregnation of triethylaluminum-pretreated silica with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$, and its use in ethylene polymerization in combination with Cp_2HfMe_2 , has been reported by Hlatky and Upton.²⁵ In this approach, use is made of the relatively poor solubility of these borates in aliphatic hydrocarbon solvents, compared with their solubility in toluene. In the present work, impregnation of a $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was effected in toluene. After removal of the solvent, contact of the solid, borate-impregnated support with the metallocene was carried out in heptane.

This article outlines the preparation and use in ethylene and propylene polymerization of MgCl_2 -immobilized borate activators in combination with zirconocene catalysts. It is seen that in the case of the chemical tethering of borate activator to the support, the use of $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ gives significantly higher catalyst activity than obtained using SiO_2 pretreated with AlEt_3 . High activity is obtained using $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ simply impregnated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, although the particle morphology of the resulting polymers is seen to be inferior to that obtained in the case of the tethered borate.

EXPERIMENTAL

Materials

All manipulations were performed under an argon atmosphere using glove box (Braun MB-150 GI or LM-130) and Schlenk techniques. Solvents were distilled from Na (toluene) or Na/benzophenone (heptane) and freeze-thaw degassed twice before use.

Petroleum ether (bp 40–70°C) was passed over a column containing Al_2O_3 and stored over 4 Å molecular sieves.

rac-Ethylenebis(indenyl)zirconium dichloride $[\text{Et}(\text{Ind})_2\text{ZrCl}_2]$ ²⁶ and *rac*-dimethylsilylbis(2-methyl-1-indenyl) zirconium dichloride $[\text{Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrCl}_2]$ ²⁷ were prepared following published procedures, as was the corresponding dimethyl derivative $[\text{Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrMe}_2]$.²⁸ $[\text{Cp}_2\text{ZrMe}_2]$ was obtained by reaction of $[\text{Cp}_2\text{ZrCl}_2]$ with methyllithium.²⁹

AlEt_3 (25 wt % solution in toluene) and $\text{Al}i\text{Bu}_3$ (1M solution in hexane) were purchased from Aldrich and Fluka, respectively.

Ethylene (3.5 grade supplied by Air Liquide) and propylene (3.5 grade supplied by Hoek Loos) were purified by passing over columns of BASF RS3–11 supported Cu oxygen scavenger and 4 Å molecular sieves.

$[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$ was prepared using a modified method, following procedures described in refs. 22 and 23. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was prepared following previously published procedures.^{30,31}

Catalyst support preparation and borate immobilization

The $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support used in this study was prepared by gradual addition (over 5–10 min) of a 25 wt % solution of AlEt_3 in toluene to 10 g of a spherical adduct of magnesium chloride and ethanol ($\text{MgCl}_2 \cdot 2.1 \text{ EtOH}$), slurried in 200 mL heptane, and cooled to 0°C, to give a mol ratio $\text{AlEt}_3/\text{EtOH} = 2$. The reaction was carried out in a standard Schlenk vessel equipped with a pressure release valve. After 2 days at ambient temperature, with occasional agitation, the solid support was isolated by filtration, washed with heptane and petroleum ether, and then dried under a flow of argon and subsequently in vacuum. Analysis of the support composition was carried out as described previously.^{6–9}

A reference AlEt_3 -pretreated silica support was prepared by gradual addition (5–10 min) of 6 mL of 25 wt % AlEt_3 in toluene to a slurry of 2 g Sylopol 948 silica (Grace GmbH), precalcined at 600°C for 3 h, in 20 mL heptane cooled to 0°C, again in a standard Schlenk vessel equipped with a pressure release valve. The slurry was agitated for a further 4 h and then filtered, washed four times with 10 mL heptane and dried in vacuum.

Immobilization of $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$ was carried out by heating 0.07 g of the borate in 7 mL toluene at 85°C to effect dissolution, after which the solution was added to a slurry of 1 g of the support ($\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ or AlEt_3 -pretreated SiO_2) in toluene (18 mL). The mixture was kept at 75°C for 35 min. After allowing to cool under argon, the slurry

was placed in a shaker for 2.5 h before drying in vacuum to give a free-flowing powder.

Immobilization of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was carried out by contacting the $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support (1 g) with a solution of the borate (91 mg; 100 μmol) in 2 mL toluene at room temperature. After agitating the mixture for 30 min, the solvent was removed at 50°C under a flow of argon, followed by vacuum (2 h), yielding a yellow, free-flowing solid. Single-site catalyst immobilization was carried out by contacting 100 mg of the borate-impregnated support with between 3 and 10 μmol catalyst ($[\text{Cp}_2\text{ZrMe}_2]$ or *rac*- $[\text{Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrMe}_2]$) in heptane for 30 min. The solvent was then removed under a flow of argon and the solid dried under vacuum for 30 min, then washed twice with 1–2 mL of petroleum ether and dried again. The solid was reslurried in 5 mL petroleum ether prior to injection into the polymerization reactor.

Polymerization conditions

Polymerizations using supports treated with $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$ were carried out in a 200-mL Büchi reactor equipped with a hollow-shaft turbine stirrer. Hundred milligrams of the borate-treated support was charged to the reactor, followed by a catalyst solution containing 2.4 μmol *rac*- $[\text{Et}(\text{Ind})_2\text{ZrCl}_2]$ and obtained by addition of 1 mL of a 28 wt % solution of triisobutylaluminum in hexane to a solution of 2 mg of *rac*- $[\text{Et}(\text{Ind})_2\text{ZrCl}_2]$ in 4 mL toluene and ageing for 75 min. This corresponded to a B/Zr mol ratio of 4. The support/catalyst mixture was allowed to stand for 60 min, after which 100 mL heptane, containing 1 mL of a 28 wt % solution of triisobutylaluminum in hexane, was added under an atmosphere of monomer. The reactor was heated to 50°C and pressurized with 0.5 bar of monomer for 15 min before raising the pressure to 0.4 MPa and polymerizing at a constant pressure of 0.4 MPa for 1 h. The polymerization was terminated by degassing the reactor, followed by the addition of acidic methanol.

Polymerizations using supports treated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ were carried out in a 1-L Premex reactor equipped with a vortex stirrer, preheated overnight at 60°C under vacuum and purged with argon. Petroleum ether (450 mL) was introduced via a cannula. The reactor contents were stirred and heated to 50°C. Triisobutylaluminum (1 mmol) in petroleum ether (10 mL) was introduced via the catalyst injection system. A monomer overpressure of 0.1 MPa was applied and stirring continued for 5–10 min. The preformed catalyst slurry was introduced via the catalyst injection system, which was then flushed with a further 50 mL petroleum ether. The monomer pressure was increased to 0.5 MPa and kept constant for the duration of the polymerization, keeping the temperature at 50°C and with a stirrer speed of ~ 1000 rpm. Polymer-

ization was terminated by injection of 20 mL methanol. After venting the reactor, the polymer slurry was mixed with 20 mL ethanol containing 10% HCl, followed by 200 mL ethanol, and stirred for 20 min. The polymer was recovered by filtration, washed with water (3×100 mL) and ethanol (2×30 mL) and dried in vacuum overnight at 70°C.

Polymer characterization

Molecular weights and molecular weight distributions of the resulting polymers were determined by high temperature GPC (PL-GPC210) at 135°C, using 1,2,4-trichlorobenzene as solvent.

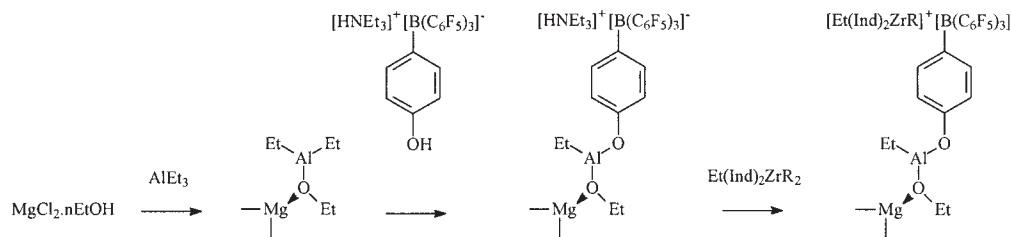
DSC analysis was carried out using a Thermal Analysis DSC Q100 from TA Inc. in the standard DSC run mode, under nitrogen atmosphere. Calibration was carried out using an indium standard at a heating rate of 10°C/min. The polymer sample, 4–6 mg, was heated from 50 to 180°C at a rate of 10°C/min to remove thermal history, before cooling to 50°C at 10°C/min. A second heating cycle at 10°C/min was used for the determination of the peak melting temperature, T_{m2} .

^{13}C NMR (125.69 MHz) determination of polypropylene tacticity was carried out at 120°C using a Varian Unity Inova 500 NMR spectrometer. The polymer (150–200 mg) was dissolved in 1,2,4-trichlorobenzene (2.5 mL) and deuterated tetrachloroethane (0.5 mL) and analysis carried out in a 10-mm NMR tube at a pulse angle of 74°, acquisition time 1.3 s, and relaxation delay 4 s.

SEM characterization of polymer particle morphology was carried out using a Philips environmental scanning electron microscope (XL-30 ESEM-FEG), equipped with an energy-dispersive X-ray spectrometer for local and area distribution analyses of elements. Secondary electron imaging of the sample surfaces was performed in high vacuum mode using acceleration voltages of 1 kV. For particle cross-sectional analysis, polymer samples were embedded either in SPURR low viscosity epoxy resin (SPI Supplies) or in Jung Tissue Freezing Medium (Leica Instruments GmbH) and cut with a razor blade after cooling in liquid nitrogen. In the latter case, the freezing medium was washed away with water before the SEM imaging.

RESULTS AND DISCUSSION

The $\text{MgCl}_2/\text{Et}_n\text{Al}(\text{OEt})_{3-n}$ support used in this study, prepared by the treatment of a spherical adduct of magnesium chloride and ethanol ($\text{MgCl}_2 \cdot 2.1 \text{ EtOH}$) with triethylaluminum, was found to contain 5.2 wt % Al and 6.1 wt % residual ethoxide, indicating the overall composition $\text{MgCl}_2 \cdot 0.24 \text{ AlEt}_{2.3}(\text{OEt})_{0.7}$



Scheme 1 Immobilization of a borate-activated metallocene on a MgCl_2 -based support.

In a first approach to the immobilization of borate activators using such supports, the support was contacted with $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$. Reaction between the 4-hydroxyphenylborate moiety and the residual aluminum alkyl on the magnesium chloride support should result in the immobilization of the borate activator as illustrated in Scheme 1, assuming that the predominant reaction is between the active hydrogen of the phenol and the aluminum alkyl. It is possible, however, that the aluminum alkyl could also react with the active hydrogen present in the ammonium cation, generating a transient $[\text{AlEt}(\text{OEt})]^+$ species. Studies by Bochmann^{32,33} have shown that transient $[\text{AlR}_2]^+$ can abstract C_6F_5 from a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, leading to the formation of borane species $\text{BR}_n(\text{C}_6\text{F}_5)_{3-n}$. Götz et al.²⁰ have reported that, in the absence of a metallocene, $\text{Al}i\text{Bu}_3$ reacts with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ to give $\text{Al}i\text{Bu}_n(\text{C}_6\text{F}_5)_{3-n}$ and borane compounds. A detailed study of reactions between various aluminum alkyls and borate salts of type $[\text{HNR}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$ is in progress elsewhere and will be reported separately. (Novarino and Hessen, Manuscript in preparation.)

For the immobilization of $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$ on the $\text{MgCl}_2 \cdot 0.24 \text{AlEt}_{2.3}(\text{OEt})_{0.7}$ support, it was necessary to first solubilize the borate by heating in toluene at 75°C before mixing with the support. Ethylene and propylene polymerizations were carried out in heptane slurry, using the resulting borate-treated supports in combination with $\text{rac}[\text{Et}(\text{Ind})_2\text{ZrCl}_2]$ and triisobutylaluminum. For the purpose of comparison, reference polymerizations were carried out using a silica-immobilized borate prepared by the treatment

of AlEt_3 -pretreated SiO_2 with $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$. The results are given in Table I, from which it is apparent that in both ethylene and propylene polymerization significantly higher activities were obtained with the magnesium chloride-based support. The polymer molecular weight distributions were also somewhat narrower using this support, the results indicating effective retention of the single-site characteristics of the catalyst. ^{13}C NMR analysis of the polypropylenes revealed moderate isotacticities, the *mmmm* pentad contents for the polymers prepared using the MgCl_2 - and the SiO_2 -based supports being 77 and 88%, respectively. The lower isotacticity of the polymer prepared using the MgCl_2 -based support may be at least partly related to the higher activity of this system, resulting in an exotherm of around 5°C during polymerization. Homogeneous propylene polymerizations carried out under similar conditions with $\text{rac}[\text{Et}(\text{Ind})_2\text{ZrCl}_2]/\text{Al}i\text{Bu}_3$ -MAO have given low molecular weight polymers containing between 67 and 82% *mmmm*, the lowest isotacticity (and highest activity) being obtained at high MAO/Zr.³⁴ The DSC melting points (T_{m2}) of the polypropylenes prepared as indicated in Table I were 139 and 140°C respectively, while the two polyethylenes gave T_{m2} values of 133°C .

The polymers prepared were all free-flowing powders and there was no evidence of reactor fouling. Scanning electron micrographs of the polyethylenes obtained with MgCl_2 - and the SiO_2 -based supports are shown in Figures 1 and 2, respectively. Reasonable polymer particle morphology is apparent in each case, with the spheroidal MgCl_2 -derived polymer having the more porous particle surface. SEM images of the polypropylenes obtained with these systems are

TABLE I
Polymerizations^a Carried out Using $\text{rac}[\text{Et}(\text{Ind})_2\text{ZrCl}_2]/\text{Al}i\text{Bu}_3$, in Combination with Supports Treated with $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$

Support	Monomer	Activity (kg/(mol Zr h))	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
$\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$	Ethylene	3948	193,000	67,000	2.9
$\text{SiO}_2/\text{AlEt}_3$	Ethylene	216	277,000	77,000	3.6
$\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$	Propylene	404	45,300	26,300	1.7
$\text{SiO}_2/\text{AlEt}_3$	Propylene	160	57,000	32,000	1.8

^a Polymerization conditions: Heptane slurry, 0.4 MPa monomer pressure, 50°C , 1 h.

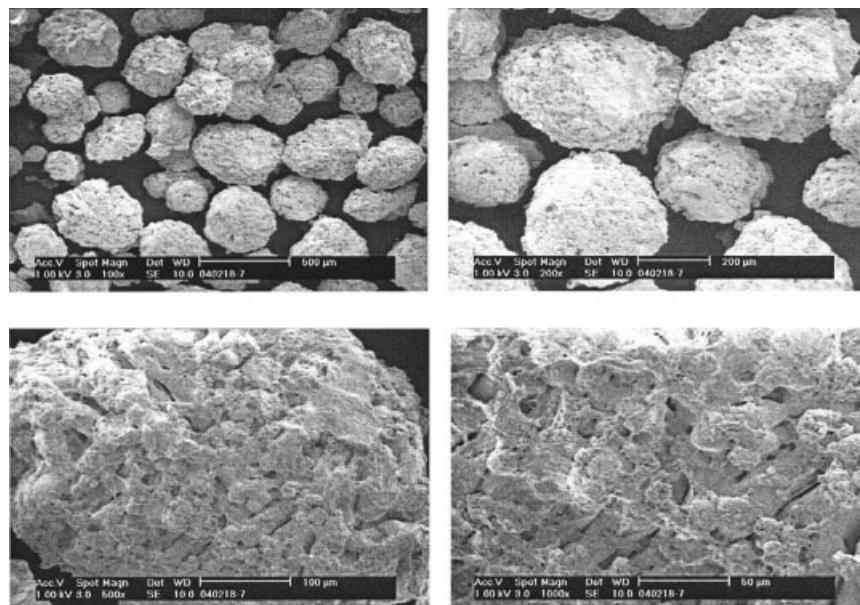


Figure 1 Scanning electron micrographs of polyethylene particles prepared as in Table I, using MgCl_2 -based support.

shown in Figures 3 and 4. It is apparent from Figure 3 that spherical particle morphology could be obtained with the MgCl_2 -based support, but Figure 4 reveals a significant loss of morphology due to particle agglomeration in the case of the polypropylene prepared using the SiO_2 support. The SEM images of the latter polymer also show the presence of white, spherical material embedded in the particle surface. Using SEM/EDX, it was established that these spheres contained aluminum, with no evidence of silicon or carbon, indicating that they were formed by hydrolysis of the scavenger ($\text{Al}(\text{iBu})_3$) during quenching at the end of

the polymerization. The partial covering of this material by polymer indicates that in this system some catalyst leaching has taken place, leading to fine particulate polymer deposition on the particle surface.

The internal particle morphologies of the polyethylenes obtained using the different supports were investigated by SEM imaging of particle cross sections, obtained after first embedding the polymers in an epoxy resin. The SEM cross-sectional images in Figure 5 reveal significant differences in the internal particle morphologies. A compact, uniform polymer morphology is apparent in the polyethylene prepared using

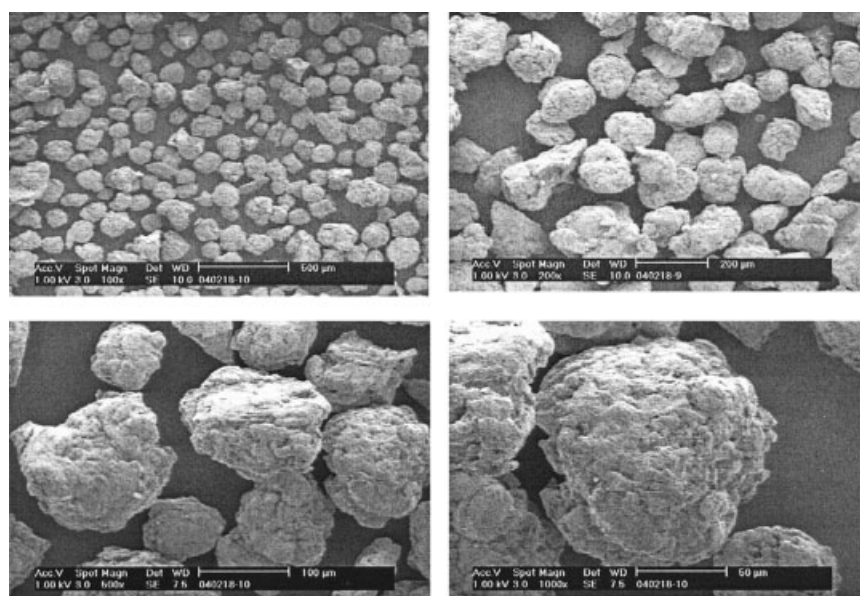


Figure 2 Scanning electron micrographs of polyethylene particles prepared as in Table I, using SiO_2 -based support.

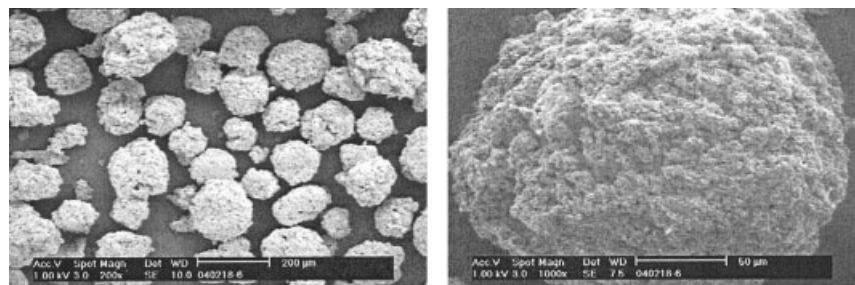


Figure 3 Scanning electron micrographs of polypropylene particles prepared as in Table I, using MgCl_2 -based support.

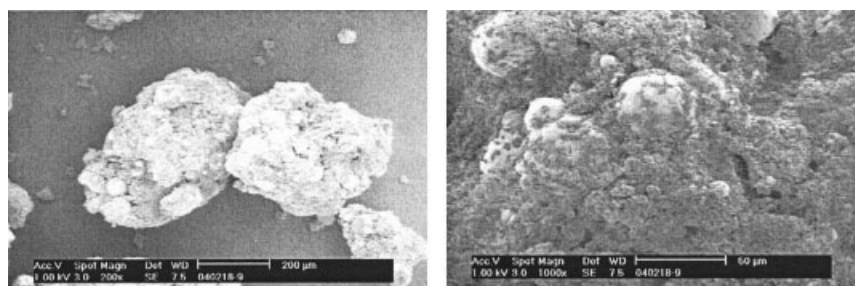


Figure 4 Scanning electron micrographs of polypropylene particles prepared as in Table I, using SiO_2 -based support.

the MgCl_2 -based support, whereas a nonuniform cross section is evident in the polymer obtained using the SiO_2 support. In the latter case, a white core of silica can be seen at the center of the particle, indicating incomplete fragmentation of the support during polymerization. It is well known that fragmentation is dependent on the nature of the support, gradual and progressive fragmentation often being observed with silica, as opposed to the relatively rapid fragmentation typical of magnesium chloride supports.³⁵ In the present work, the lower activities obtained with silica are consistent with the incomplete fragmentation of the support during the course of polymerization.

The above results confirm the feasibility of single-site catalyst immobilization and activation using a borate tethered to a $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$ support. To

determine whether effective catalyst/activator immobilization could also be achieved simply by physical impregnation on the support, a second approach was investigated in which a nontethered borate activator was used.

Impregnation of the support [$\text{MgCl}_2 \cdot 0.24 \text{AlEt}_{2.3}(\text{OEt})_{0.7}$] with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in toluene, at a level of 100 μmol borate/g support, was followed by removal of the solvent under reduced pressure. The impregnated support was recovered in the form of a yellow, free-flowing solid. The polymerizations were carried out simply by slurring the borate-impregnated support with a solution of $[\text{Cp}_2\text{ZrMe}_2]$ or *rac*- $[\text{Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrMe}_2]$ in heptane, before injection into the polymerization reactor. The polymerization results are given in Table II, from which high activities

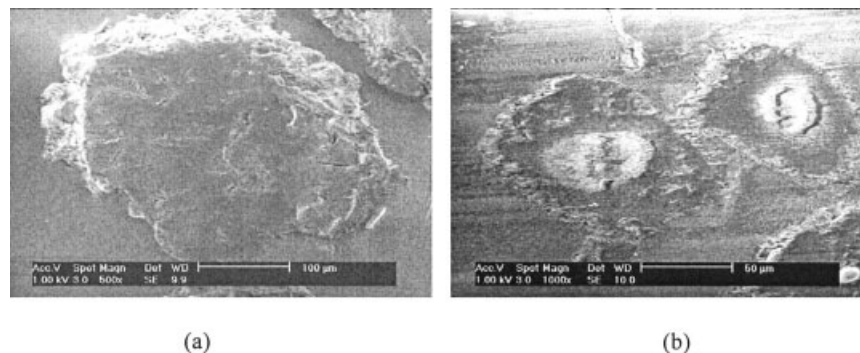


Figure 5 Cross-sectional images of polyethylene particles prepared as in Table I: (a) using MgCl_2 -based support; (b) using SiO_2 -based support.

TABLE II
 Po1ymerizations^a Carried out Using MgCl₂/AlEt_n(OEt)_{3-n} Support Impregnated with [Ph₃C][B(C₆F₅)₄].

Exp.	Metallocene	Borate	B/Zr mol ratio	Monomer	Activity kg/(mol Zr h)	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	[Cp ₂ ZrMe ₂]	[Ph ₃ C][B(C ₆ F ₅) ₄]	1	Ethylene	4,600	283,000	120,000	2.4
2	[Cp ₂ ZrMe ₂]	[Ph ₃ C][B(C ₆ F ₅) ₄]	3	Ethylene	8,849	339,000	138,000	2.5
3	[Me ₂ Si(2MeInd) ₂ ZrMe ₂]	[Ph ₃ C][B(C ₆ F ₅) ₄]	1	Propylene	5,210	144,000	78,000	1.8
4	[Me ₂ Si(2MeInd) ₂ ZrMe ₂]	[Ph ₃ C][B(C ₆ F ₅) ₄]	2	Propylene	8,253	120,000	61,000	2.0

^a Polymerization conditions: Petroleum ether slurry, 0.5 MPa monomer pressure, 50°C, 1 h.

in both ethylene and propylene polymerizations are apparent, particularly at B/Zr mol ratios >1. The GPC results reveal narrow molecular weight distributions for the polymers prepared using these systems, indicating single-site catalyst characteristics. ¹³C NMR analysis of the two polypropylene samples (exp. 3 and 4) revealed *mmmm* contents of 93 and 91%, respectively.

The particle morphology of polyethylene and polypropylene prepared using the borate-impregnated supports is shown in Figure 6. It is evident that in the case of polyethylene, prepared using [Cp₂ZrMe₂] as catalyst component, the spheroidal morphology of the original support has been largely retained and replicated in particle growth during polymerization. However, it was observed that the resulting particles of polyethylene had low mechanical strength and could be easily crushed. Cross-sectional analysis of the polymer (Fig. 7(a)) revealed an extremely porous internal particle morphology. In the case of propylene polymerization, where the same support was used in combination with *rac*-[Me₂Si(2-MeInd)₂ZrMe₂], scanning electron microscopy revealed an irregular polymer particle morphology, indicating nonuniform particle growth, possibly as a result of incomplete immobilization of the active species in this system. However, there was again no evidence of reactor fouling in these polymerizations. In contrast to the polyethylene, cross-sectional scans of polypropylene particles re-

vealed compact polymer growth throughout the whole particle. A representative scan is shown in Figure 7(b). It is also apparent from Figures 6 and 7 that the particle size of this polypropylene was smaller than that of the polyethylene, despite the higher productivity obtained in polymerization, again reflecting a more compact particle growth in propylene polymerization with the borate-impregnated supports.

CONCLUSIONS

Immobilization of a borate activator containing a functional group able to react with an aluminum alkyl can be achieved using support materials of type MgCl₂/AlR_n(OEt)_{3-n}, readily obtainable via reaction of MgCl₂/EtOH adducts with AlR₃. Immobilized borates of this type can be used in olefin polymerization in combination with zirconocene catalysts, giving narrow molecular weight distribution polymers, without reactor fouling. The polymerization activities obtained using MgCl₂-based supports were significantly higher than those obtained in comparative experiments using a silica support pretreated with AlEt₃, cross-sectional SEM indicating easier fragmentation of the MgCl₂-based support during the course of polymerization.

MgCl₂/AlR_n(OEt)_{3-n} supports can also be impregnated with a borate activator such as [Ph₃C][B(C₆F₅)₄]. The use of this system in combination with zirconocenes gives high catalyst activity, but inferior

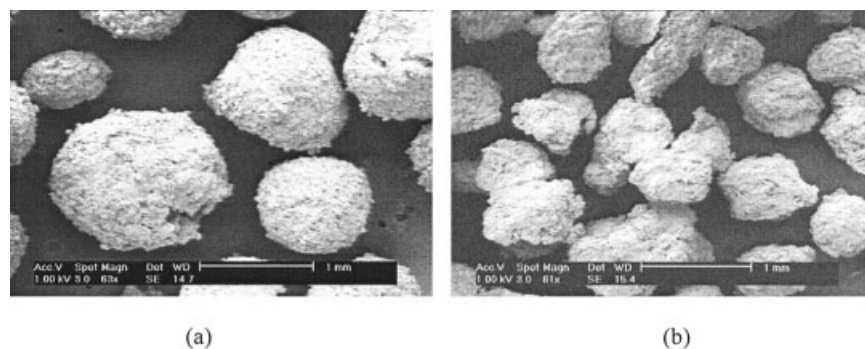


Figure 6 Scanning electron micrographs of polyethylene and polypropylene particles prepared as in Table II: (a) PE (exp. 1); (b) PP (exp. 4).

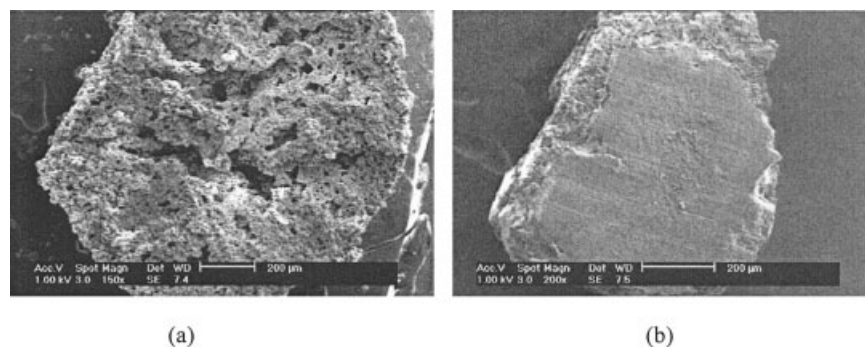


Figure 7 Cross-sectional images of polyethylene and polypropylene particles prepared as in Table II: (a) PE (exp. 1); (b) PP (exp. 4).

polymer particle morphologies compared to those obtained in the case of immobilization via reaction of $[\text{HNET}_3][\text{B}(\text{C}_6\text{F}_5)_3(\text{C}_6\text{H}_4\text{-4-OH})]$ with the support.

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