Activity
1.8 ton-PE·mmol-Zr⁻¹h⁻¹

Ethylene 0.9MPa,
0.5h, 50 °C, Toluene

MeO ... N ... ZrCl₂

**Highly Active
Zr Catalysts**

$M_n/10^3$

M_w/M_n

Polymerization time/ h

Unique Catalysis

Polymer yield

Ethylene 0.1 MPa,
75 °C

Polymerization time/ min

**Highly Controlled Living
Ti Catalysts**

Ligand

Polymer

M

n

MgCl₂/
$R'_nAl(OR)_{3-n}$

Activator/ Support

**Thermally Robust
V Catalysts**

**Highly Syndiotactic
Polypropylenes**

[rr] 97 %, T_m 155 °C,
M_w/M_n 1.16

**Distinctive
Polymer Formation**

**Peculiar Comonomer
Distribution Copolymers**

GPC-IR   Ethylene-Propylene
Copolymer

Propylene Content

Log M_w

**High Bulk-Density
Polyethylene Particles**

BD 0.50 g/m L

100 μ

**Ultra-Fine Noncoherent
Polyethylenes**

M_v 3,210,000

×1000   10 μ

MgCl$_2$/R$'_n$Al(OR)$_{3-n}$: An Excellent Activator/Support for Transition-Metal Complexes for Olefin Polymerization

Yasushi Nakayama, Junji Saito, Hideki Bando, and Terunori Fujita*[a]

Dedicated to Dr. Norio Kashiwa, the inventor of MgCl$_2$-supported TiCl$_4$ catalysts, on the occasion of his award of the Medal with Purple Ribbon from the Government of Japan

Abstract: A new and effective method for the activation, and simultaneously, immobilization of bis(phenoxyimine) early-transition-metal complexes for olefin polymerization (known as FI catalysts), which makes use of MgCl$_2$/R$'_n$Al(OR)$_{3-n}$ as an activator/support, has been developed. Ti-, Zr-, and V-FI catalysts combined with this MgCl$_2$-based compound can form highly active MgCl$_2$-supported single-site catalysts capable of demonstrating superior catalytic properties, compared to the corresponding homogeneous methylaluminoxane- (Ti- and Zr-FI catalysts) or alkylaluminum-activation systems (V-FI catalysts), in terms of their catalytic activity, molecular weight, stereoselectivity, and comonomer incorporation. Additionally, these new catalysts can produce polymers of significant morphology with high efficiency. Notably, the MgCl$_2$-based compounds can also effectively activate and immobilize the early-to-late transition-metal complexes that have emerged recently. Thus, the application of MgCl$_2$-based compounds as activators/supports for transition-metal complexes for olefin polymerization provides a conceptually new strategy for the development of methylaluminoxane- and borate-free, high-performance, single-site catalysts capable of controlling polymer morphology.

Keywords: activators · FI catalysts · polymerization · polyolefins · supported catalysts

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Introduction

The discovery and application of TiCl$_4$/alkylaluminum/ MgCl$_2$ catalyst systems (MgCl$_2$-supported TiCl$_4$ catalysts) have revolutionized the polyolefin manufacturing industry.[1] The extremely high activity and stereoselectivity of these catalysts have given rise to simplified, environmentally benign production processes and the formation of reasonably priced polyolefins with improved performance parameters. Moreover, it should be stressed that the use of MgCl$_2$-supported catalysts has enabled excellent control of the polymer morphology, due to the ease with which MgCl$_2$-supports with controlled particle sizes and narrow particle size distributions can be prepared, and this has contributed significantly to the enhancement of polymer productivity.

While these supported catalysts are the pillars of the polyolefin industry, because of the above-mentioned advantages, they are multisite catalysts consisting of many types of uncharacterized active sites that form polymers with broad distributions of molecular weight and chemical composition. Therefore, it is very difficult to precisely control the polymer microstructure and hence the properties of the resulting polymers when using these multisite catalysts. Though extensive and continuous efforts have been devoted to developing MgCl$_2$-supported single-site TiCl$_4$ catalysts,[2] no single-site catalyst of this type has been reported thus far.

Although MgCl$_2$ was originally introduced as a support, kinetic studies have revealed that MgCl$_2$ not only increases the number of active sites, as intended, but also enhances the rate constant for chain propagation.[3] This shows that MgCl$_2$ functions as an activator for Ti chloride species as well as a support. Whereas its high performance as a support has been well documented, the fact that MgCl$_2$ works as a good activator for Ti chloride species has often been overlooked.[4] We have argued that the unexpected function of MgCl$_2$ as an activator stems from an electronic interaction between a catalytically active Ti chloride species and

MgCl$_2$.[12,13] The electronic interaction may reduce the energy barrier to olefin insertion, together with immobilization of the catalytically active species on MgCl$_2$.

Group 4 metallocene complexes combined with methylaluminoxane (MAO) or borate activators (metallocene catalysts) are highly active, single-site catalysts, and hence have been used to create a wide variety of unique polymers, which possess controlled microstructures and related properties, with high efficiency.[5] Some attempts have been made to use a MgCl$_2$-based compound as an activator for Group 4 metallocene complexes to develop MAO- and borate-free, highly active single-site catalysts.[6] The results, however, have so far not been good, in particular, with respect to catalytic activity when compared with MAO or borate activation. We have inferred that the absence of heteroatoms in the ligands, capable of inducing an effective electronic interaction with MgCl$_2$, is responsible for the limited success in the application of MgCl$_2$-based compounds as the activator for Group 4 metallocene complexes.[12,13]

With recent advances in the rational design of well-defined transition-metal complexes for olefin polymerization, quite a few new highly active single-site catalysts, based on both early and late transition-metal complexes, have been developed, which typically contain heteroatom-based ligands, such as diimine, diiminepyridine, phenoxyimine, diamide, phosphineimide, and bis(phenoxy)amine ligands.[7] Some of these complexes, when activated, can form unique polymers (e.g., hyper-branched polyethylenes (PEs), ethylene–polar-monomer copolymers, and polyolefinic block copolymers) that are difficult to produce with metallocene catalysts. Additionally, we have developed a series of highly active transition-metal complexes for olefin polymerization, represented by bis(phenoxyimine) early-transition-metal complexes (FI catalysts), bis(pyrrolideimine) Group 4 transition-metal complexes (PI catalysts), and bis(indolideimine) Ti complexes (II catalysts).[8–11] These complexes combined with an appropriate activator display unique polymerization catalysis and form distinctive polymers (e.g., vinyl-terminated PEs; highly syndiotactic and isotactic polypropylenes (PPs); Al-terminated PEs; regio- and stereoirregular high-molecular-weight poly(1-hexene)s; and block copolymers from ethylene, propylene, norbornene and higher α-olefins). Comprehensive reviews charting the development and appli-

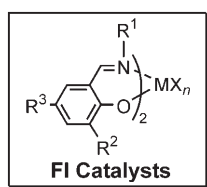cation of the above transition-metal complexes for olefin polymerization are available.[7,8]

Unlike Group 4 metallocene complexes, these new transition-metal complexes contain heteroatoms in the ligands, which may induce an effective interaction with MgCl$_2$. Accordingly, we believed that the combination of MgCl$_2$ and the above transition-metal complexes could generate highly active single-site catalysts. Additionally, we anticipated that the electronic interaction may lead to the immobilization of an active species, resulting in an MgCl$_2$-supported catalyst. We discovered that MgCl$_2$/R'$_n$Al(OR)$_{3-n}$ is not only highly effective for the activation but also for the immobilization of the transition-metal complexes described above, leading to the formation of highly active, supported single-site catalysts that exhibit distinctive catalysis and can furnish unique polyolefinic materials.[12,13] Chadwick et al. and Mao et al. have recently reported on a relevant MgCl$_2$-based compound, [MgCl$_2$/R$_n$Al(OEt)$_{3-n}$, R = Et, iBu], that can also act as a good activator/support for FI catalysts, diimine-ligated Ni complexes, diiminepyridine-ligated Fe complexes and others,[14] further demonstrating the high potential of MgCl$_2$-based compounds as activators/supports for transition-metal olefin polymerization catalysts.

In this article, we describe the new supported catalysts composed of recently emerging transition-metal complexes (mainly focusing on FI catalysts) and MgCl$_2$/R'$_n$Al(OR)$_{3-n}$, which are capable of providing very high activities along with good polymer morphology and retention of single-site catalysis. The new catalysts represent the first examples of MAO- and borate-free, highly active, supported single-site catalysts for olefin polymerization.

Catalytic Properties of FI catalysts with MgCl$_2$-Based Compounds

The FI catalysts that are introduced in the following sections are collected in Table 1. For the syntheses of these FI catalysts and their catalytic properties with MAO or borate activation, the reader is referred to the reviews and original papers that are summarized in references [8–11].

Table 1. Structures of FI catalysts **1**–**13**.

FI Catalysts

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
M	Ti	Ti	Ti	Ti	Ti	Ti	Zr	Zr	Zr	Zr	Zr	Zr	V
R^1	C$_6$H$_5$	C$_6$H$_5$	C$_6$H$_5$	C$_6$H$_5$	C$_6$F$_5$	C$_6$F$_5$	C$_6$H$_5$	2-Me-cyclohexyl	2-Me-cyclohexyl	2-Me-cyclohexyl	2-Me-cyclohexyl	n-hexyl	C$_6$H$_5$
R^2	tBu	tBu	tBu	tBu	Me	SiMe$_3$	tBu	cumyl	1,1-diphenylethyl	cumyl	1,1-diphenylethyl	cumyl	H
R^3	H	MeO	H	H	H	H	H	Me	MeO	MeO	H	H	H
X$_n$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	Cl$_2$	=O

Ethylene polymerization using Ti- and Zr-FI catalysts with MgCl$_2$/Et$_3$Al: Ethylene polymerizations with common FI catalysts (**1** and **7**, Table 1) were performed in the absence and presence of mechanically pulverized MgCl$_2$ (vibromill, 8 h, crystallite size 80 Å) in an effort to evaluate the potential of MgCl$_2$ as an activator for heteroatom-based transition-metal complexes for olefin polymerization.[13] Et$_3$Al was used as an alkylating agent for the FI catalysts employed to form diethylated complexes, as well as being an impurity scavenger in the polymerization systems. The results of the polymerization experiments are listed in Table 2. For comparison, the relevant results with typical Group 4 metallocene complexes, [MCl$_2$(Cp)$_2$] (M=Ti, Zr), are also included in Table 2.

Table 2. Ethylene polymerization results for FI catalysts **1**, **7**, and [MCl$_2$(Cp)$_2$] (M=Ti, Zr) with Et$_3$Al or Et$_3$Al/MgCl$_2$.[a]

	Complex ([μmol])	MgCl$_2$ [mmol]	Et$_3$Al [mmol]	Yield [g]	Activity[b]	M_v[c] (×10^3)
1	**1** (2.0)	0.4	0.4	0.32	0.3	2,430
2	**1** (2.0)	0	0.4	trace		
3	[TiCl$_2$(Cp)$_2$] (2.0)	0.4	0.4	trace		
4	**7** (8.0)	1.6	0.2	9.10	3.4	710
5	**7** (8.0)	0	0.2	trace		
6	[ZrCL2(Cp)$_2$] (8.0)	1.6	0.2	trace		

[a] Conditions: toluene (500 mL), ethylene (0.9 MPa), 50 °C, 30 min (entries 1–3), 20 min (entries 4–6). [b] kg PE (mmol metal)$^{-1}$ h^{-1}. [c] Calculated with the following equation: $[\eta]=6.2\times10^{-4}M_v^{0.7}$ ($[\eta]$=intrinsic viscosity, which was measured in decalin at 135 °C).

While the FI catalysts **1** and **7** in combination with Et$_3$Al exhibited virtually no reactivity toward ethylene, with MgCl$_2$/Et$_3$Al they were able to polymerize ethylene to high-molecular-weight PEs (viscosity-average molecular-weight (M_v), **1**: 2430000, **7**: 710000). The catalytic activities displayed by these MgCl$_2$-containing catalyst systems were 0.3 (**1**/MgCl$_2$/Et$_3$Al) and 3.4 kg PE (mmol metal)$^{-1}$ h^{-1} (**7**/MgCl$_2$/Et$_3$Al), which are very high for MAO- and borate-free catalysts based on well-defined transition-metal complexes. These results suggest that MgCl$_2$ possesses good potential as an activator for Ti- and Zr-FI catalysts, as expected. The MgCl$_2$ that is used probably acts as a Lewis acid to generate a cationic active species from the diethylated FI catalyst and becomes an anionic species, which serves as a counteranion to the cationic active species.[15]

The data summarized in Table 2 confirmed that [TiCl$_2$(Cp)$_2$] or [ZrCl$_2$(Cp)$_2$] (Cp=cyclopentadiene) with Et$_3$Al/MgCl$_2$ had very low activity (<0.1 kg PE (mmol metal)$^{-1}$ h^{-1}) under the same conditions. These facts are consistent with the proposal that MgCl$_2$ can be a useful activator for transition-metal complexes with heteroatom-containing ligands.

Preparation of MgCl$_2$ for this research: Given the promising performance of mechanically pulverized MgCl$_2$ as an activator for the common Ti- and Zr-FI catalysts, we decided to investigate MgCl$_2$ with various FI catalysts. Although both

mechanical and chemical routes are available for the production of MgCl$_2$, it is known that chemical routes, in particular, the de-alcoholysis of an MgCl$_2$/alcohol adduct (alcohol; e.g., MeOH, EtOH, nPrOH, 2-ethyl-1-hexanol) with an alkylaluminum compound (e.g., R$_3$Al, R$_2$AlCl) can form highly porous MgCl$_2$ with a small particle size, which would be a more suitable activator than mechanically pulverized MgCl$_2$. Additionally, this de-alcoholysis method is relatively easy and scalable. Therefore, for the method used to prepare MgCl$_2$ for this research we employed the reaction of a MgCl$_2$/2-ethyl-1-hexanol adduct with iBu$_3$Al or Et$_3$Al, leading to the formation of MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ or MgCl$_2$/Et$_n$Al(OR)$_{3-n}$ (OR: 2-ethyl-1-hexoxy group).[12a,13]

The resulting iBu$_n$Al(OR)$_{3-n}$ or Et$_n$Al(OR)$_{3-n}$ species such as iBu$_2$Al(OR) or Et$_2$Al(OR) would function as an in situ alkylating agent for the FI catalysts, as well as being a scavenger in the polymerization system, in a similar way to Et$_3$Al in the FI catalysts/MgCl$_2$/Et$_3$Al systems that were discussed above. The olefin polymerizations that are introduced in this paper were conducted using the resultant mixture from the reaction between an MgCl$_2$/2-ethyl-1-hexanol adduct and iBu$_3$Al or Et$_3$Al, unless otherwise stated.

X-ray analysis revealed the generation of MgCl$_2$ with a smaller crystallite size than mechanically pulverized MgCl$_2$, as anticipated (e.g., 28 Å, de-alcoholysis with iBu$_3$Al). The particle sizes of the resultant MgCl$_2$-based solid products are typically in the range of 1–15 μm (Figure 1), depending on

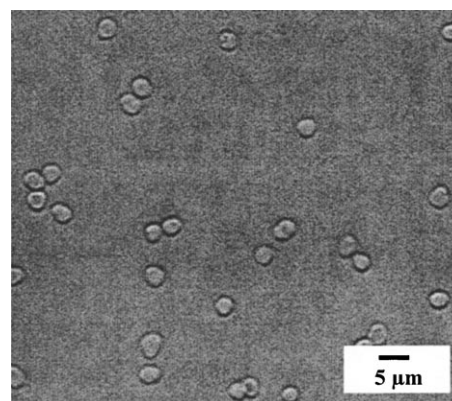Figure 1. Example of MgCl$_2$/Et$_n$Al(OR)$_{3-n}$ employed in this study.

the conditions used for the de-alcoholysis.[12b,d,13] It should be noted that some R′$_n$Al(OR)$_{3-n}$ remains in the solid product even after filtration and a thorough washing (e.g., MgCl$_2$/Et$_n$Al(OR)$_{3-n}$, R=2-ethyl-1-hexyl; MgCl$_2$·0.16 [Et$_{1.16}$Al(OR)$_{1.84}$]). The residual R′$_n$Al(OR)$_{3-n}$ may be fixed to the MgCl$_2$ probably by coordinative fixation of the type Mg-O(R)-Al and/or Mg-Cl-Al.

Ti-FI catalysts with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$: The ability of Ti-FI catalysts **1–4** (Table 1) in association with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ to mediate the polymerization of ethylene was studied (0.9 MPa ethylene pressure, 50 °C, 30 min).[13a] Table 3 summarizes the polymerization results, and also con-

Table 3. Ethylene polymerization results for FI catalysts **1–4** with various activators.[a]

	Complex	Mg [mmol]	Yield [g]	Activity[b]	M_w[c] (×10³)	M_w/M_n[c]
1[d]	**1**	0.4	9.07	36.3	509	2.66
2[d]	**2**	0.4	6.54	26.2	1170	3.51
3[d]	**3**	0.4	5.21	20.8	596	2.67
4[d]	**4**	0.4	9.01	36.0	231	2.40
5[d]	[TiCl$_2$(Cp)$_2$]	0.4	0.57	2.3	813	5.74
6[e]	**1**	0	trace			
7[f]	**1**	0	trace			
8[g]	**1**	0	11.16	44.6	464	2.38
9[g]	**2**	0	17.01	68.0	422	4.74
10[g]	**3**	0	5.35	21.4	625	2.74
11[g]	**4**	0	24.77	99.1	229	2.07
12[g]	[TiCl$_2$(Cp)$_2$]	0	6.01	24.0	1105	4.22

[a] Conditions: toluene (500 mL), complex (0.5 μmol), ethylene (0.9 MPa), 50°C, 30 min. [b] kg PE (mmol metal)$^{-1}$ h^{-1}. [c] Determined by GPC using polyethylene calibration. [d] MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ prepared by the de-alcoholysis of an MgCl$_2$/6(2-ethyl-1-hexanol) (0.4 mmol as MgCl$_2$) with iBu$_3$Al (2.4 mmol). [e] iBu$_n$Al(OR)$_{3-n}$ synthesized by the reaction of 2-ethyl-1-hexanol (2.4 mmol) with iBu$_3$Al (2.4 mmol). [f] iBu$_3$Al (2.4 mmol). [g] MAO (1.25 mmol) as Al.

tains the results for these FI catalysts combined with MAO, iBu$_n$Al(OR)$_{3-n}$ or iBu$_3$Al for comparison.

As anticipated, these Ti-FI catalysts with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ show significant activity, compared to those with iBu$_n$Al(OR)$_{3-n}$ or iBu$_3$Al, which only afforded small quantities of product. These results indicate that MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ is a highly effective activator for Ti-FI catalysts, resulting in the realization of MAO- and borate-free highly active FI catalysts. While MgCl$_2$ is unambiguously a pivotal component of the activator, the possibility cannot be ruled out that iBu$_n$Al(OR)$_{3-n}$-coordinated MgCl$_2$ plays a role in the achievement of very high catalytic activity, which will be the subject of further investigation in our laboratory.

The activities obtained with the Ti-FI catalyst **1–4**/MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ systems (20.8–36.3 kg PE (mmol metal)$^{-1}$ h^{-1}) are comparable to or surpass those seen with the highly active [TiCl$_2$(Cp)$_2$]/MAO catalyst system. Significantly, the activities exhibited by the MgCl$_2$-based activator systems compare with those observed for the well-established MAO activator systems. These results suggest the very high potential of MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ as an activator for Ti-FI catalysts. It should be pointed out that [TiCl$_2$(Cp)$_2$] with this MgCl$_2$-based compound exhibited a substantially lower activity than that with MAO activation by a factor of about 1/10 under the same conditions.[16] We reasoned that the poor performance of this MgCl$_2$-based activator for [TiCl$_2$(Cp)$_2$] originates from the fact that [TiCl$_2$(Cp)$_2$] does not contain heteroatoms in the ligand. Chadwick and co-workers have recently reported that [TiCl$_3$(Cp)] combined with an MgCl$_2$-based compound exhibits far higher ethylene polymerization activity than [TiCl$_2$(Cp)$_2$] with the same MgCl$_2$-based compound under identical conditions; this result suggests that MgCl$_2$ might probably be a better activator for heteroatom-based transition-metal complexes.[14b]

Figure 2 reveals that the PEs produced with Ti-FI catalysts **1–4**/MgCl$_2$-based compounds display morphologies with well-defined particles, whereas that formed with the MAO-activation systems leads to stringy materials that ex-
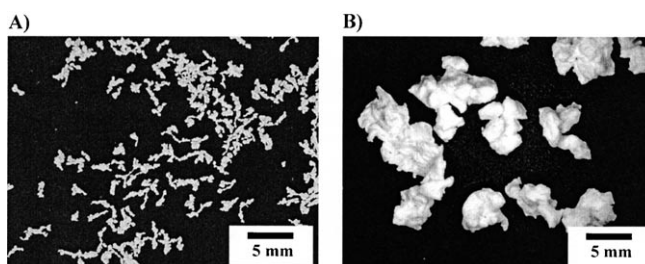

Figure 2. Photographs of the PEs produced with FI catalyst **4** using A) MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ and B) MAO as an activator.

hibit ill-defined polymer morphologies. These observations indicate that the Ti-FI catalysts are immobilized on the surface of the solid MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ activator, and hence the polymerization takes place on the solid surface (MgCl$_2$-supported catalysts). The electronic interaction between the catalytically active species and MgCl$_2$ evidently accounts for the immobilization of the catalysts onto the MgCl$_2$. The results described above demonstrate that MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ functions as a good activator and a support for Ti-FI catalysts, as does MgCl$_2$ for the industrially dominant MgCl$_2$-supported TiCl$_4$ catalysts.

It is known that the morphology of the polymer particles can be controlled by the form of the support used (i.e., the particle morphology of the starting support is retained and replicated during the course of polymerization).[4,5g] Additionally, a variety of MgCl$_2$-supports with controlled particle sizes and narrow particle size distributions are available with the de-alcoholysis method. Therefore, these MgCl$_2$-supported catalyst systems have a significant technological advantage vis-à-vis control over the polymer morphology, which is essential for commercial applications.

Although the Ti-FI catalyst **2** system provided a PE with a relatively broad molecular-weight distribution (M_w/M_n) of 3.51 [which is narrower than that for the corresponding MAO-activation system (M_w/M_n 4.74)], the PEs arising from the Ti-FI catalysts **1**, **3** and **4**/MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ systems have narrow molecular-weight distributions (M_w/M_n 2.40–2.67). These results suggest that Ti-FI catalysts can maintain single-site characteristics after immobilization.

Ethylene/propylene copolymerization with the MgCl$_2$-supported Ti-FI catalyst **4** (conditions; 50°C, 30 min, 0.9 MPa total pressure) was carried out to further confirm the single-site behavior of the MgCl$_2$-supported Ti-FI catalyst systems. This catalyst system generated an amorphous copolymer possessing a propylene content of 29 mol% with a high activity of 28 kg polymer (mmol metal)$^{-1}$ h^{-1}. GPC-IR analysis revealed the formation of a copolymer with a narrow molecular-weight distribution (M_w/M_n 1.70) and with evenly distributed propylene units along the polymer chain (Figure 3).
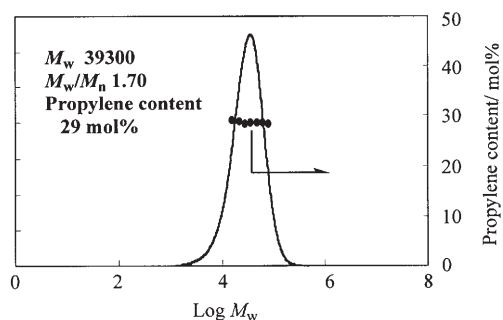
Figure 3. GPC-IR chart of the ethylene–propylene copolymer produced with MgCl$_2$-supported Ti-FI catalyst **4**.

The polymerization results described so far show that the MgCl$_2$-supported Ti-FI catalysts are highly active single-site catalysts, representing the first examples of such catalysts free of MAO and borate.

MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ was also examined as an activator/support for living Ti-FI catalysts **5** and **6** (Table 1), which induce room-temperature living propylene polymerization upon activation with MAO.[9g] Notably, the propylene polymerizations with these catalyst systems proved to retain the desired living characteristics and formed PPs with extremely narrow molecular-weight distributions (25 °C, atmospheric pressure, **5**; M_w/M_n 1.09, M_n 53000, **6**; M_w/M_n 1.16, M_n 22500). The living nature was confirmed by the linear correlation between M_n and the polymerization time, coupled with the narrow M_w/M_n values that were observed. These are the first examples of living olefin polymerization mediated by a MAO- and borate-free, Group 4 metal-based catalyst system. To our surprise, Ti-FI catalyst **6** with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ afforded a higher tacticity PP with a higher peak melting temperature ([rr] 97 %, T_m 155 °C) (Figure 4) than the corresponding MAO-activation system ([rr] 93 %, T_m 152 °C).[9g]

This is of great significance, since supported transition-metal olefin polymerization catalysts normally display lower stereoselectivities and T_ms than those of solution phase analogues. The T_m value of 155 °C represents one of the highest known values for PPs synthesized at room temperature.[17]
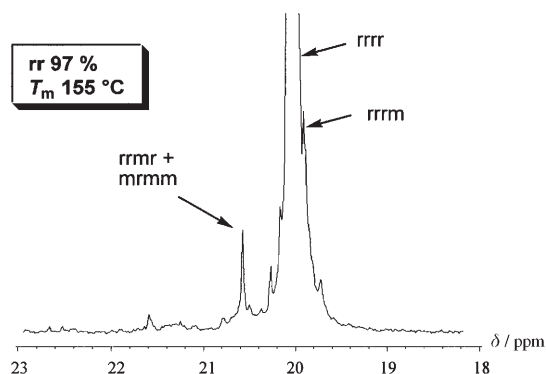

Figure 4. ^{13}C NMR spectrum of the methyl pentad region for the sPP formed with MgCl$_2$-supported Ti-FI catalyst **6**.

Zr-FI catalysts with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$: Zr-FI catalysts **7–10** (Table 1) combined with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ were investigated for their potential as ethylene polymerization catalysts.[13c] Polymerization results are compiled in Table 4.

Table 4. Ethylene polymerization results for FI catalysts **7–10** with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ or MAO.[a]

	FI catalyst	Mg [mmol]	Yield [g]	Activity[b]	M_v[c] ($\times 10^3$)
1[d]	**7**	0.20	1.96	245	91
2[d]	**8**	0.20	8.67	1084	4100
3[d]	**9**	0.20	8.00	1000	4600
4[d]	**10**	0.20	14.55	1819	5090
5[e]	**7**	0	10.29	1286	74
6[e]	**8**	0	6.02	753	2130
7[e]	**9**	0	11.91	1489	2980
8[e]	**10**	0	13.14	1643	3990

[a] Conditions: toluene (500 mL), FI catalyst (0.016 μmol), ethylene (0.9 MPa), 50 °C, 30 min. [b] kg PE (mmol metal)$^{-1}$h^{-1}. [c] Calculated with the following equation: $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$ ($[\eta]$ = intrinsic viscosity, which was measured in decalin at 135 °C) [d] MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ prepared by the de-alcoholysis of an MgCl$_2$/3(2-ethyl-1-hexanol) (0.2 mmol as MgCl$_2$) with iBu$_3$Al (0.8 mmol). [e] MAO (1.25 mmol) as Al.

It is evident that extremely high catalytic activities (245–1819 kg PE (mmol metal)$^{-1}$h^{-1}) are achieved with these catalyst systems, representing some of the highest activities for ethylene polymerization catalysts ever recorded. In fact, to the best of our knowledge, the activity demonstrated by FI catalyst **10** with this MgCl$_2$-based compound, 1819 kg PE (mmol metal)$^{-1}$h^{-1}, is the highest activity for MAO- and borate-free olefin polymerization catalysts. It is highly significant that the activities for Zr-FI catalysts **8** and **10** combined with MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ compare favorably with those found for MAO-activator systems.

As anticipated, the PEs formed with the Zr-FI catalysts **7–10**/MgCl$_2$/iBu$_n$Al(OR)$_{3-n}$ display a well-defined particle morphology, confirming that these systems are also MgCl$_2$-supported catalysts. GPC analysis reveals that the PE produced by MgCl$_2$-supported Zr-FI catalyst **7** has a broad molecular-weight distribution (M_w/M_n 13.16, M_w 51300), indicative of the presence of multiple active species in this catalyst system. Taking into account the fact that an FI catalyst potentially forms five cationic species arising from different modes of ligand coordination, the production of PEs with broad molecular-weight distributions is unsurprising. Indeed, the corresponding homogeneous MAO-activation system (**7**/MAO) forms a PE with a broad molecular-weight distribution (M_w/M_n 13.36) under identical conditions.[18] We were not able to determine the molecular-weight distributions (M_w/M_n) of the PEs formed from the Zr-FI catalysts **8–10** systems, because of their ultra-high molecular weights (M_v > 4 000 000), which are some of the highest values reported so far.

It should be noted that the PEs made with the MgCl$_2$-supported Zr-FI catalysts **8–10** possess significantly higher molecular weights than those arising from the MAO-activated homogeneous systems. While the reason for the increase in product molecular weight as a result of the immobilization

is unclear at the present time, the immobilization might result in an increase in the amount of catalytically active species that form higher molecular-weight PEs.[9f] Chadwick et al. have observed that the immobilization of a Ti complex onto an MgCl₂-based compound can have an influence on the ligand coordination mode of the catalyst.[14b,c]

The combination of a Zr-FI catalyst and isolated MgCl₂/Et$_n$Al(OR)$_{3-n}$[19] has opened an extraordinary opportunity for the highly efficient preparation of spherical particle PEs with good polymer morphology.[12] For example, Zr-FI catalyst **11** (Table 1) coupled with MgCl₂/Et$_n$Al(OR)$_{3-n}$ enables us to produce spherical particle PEs with very high molecular weight (M_v 3 000 000) and with an exceptionally high bulk density of 0.50 g mL^{-1} (Figure 5), which is probably the
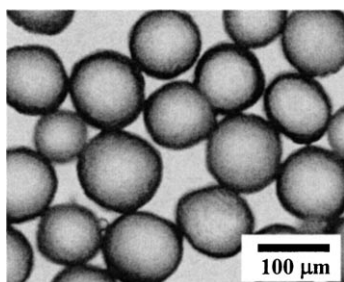
Figure 5. Photograph of the spherical particle PEs formed with MgCl₂-supported Zr-FI catalyst **11**.

highest bulk density ever achieved for PEs. The very high molecular-weight PEs can be used in applications such as artificial bones, artificial legs, and bulletproof vests, which require high strength.

In addition, the combination of a Zr-FI catalyst with an ultra-fine particle MgCl₂ support can yield unprecedented polyethylenic materials.[12d] For instance, Zr-FI catalyst **11** supported on isolated MgCl₂/iBu$_n$Al(OR)$_{3-n}$ (particle size 1.5 μm) creates very high-molecular-weight PEs consisting of noncoherent, spherical particles of 10 microns in diameter (Figure 6). Such PEs should expand the utility of polyethylenic materials (e.g., sintered filters, light diffusion films, cosmetics).

With the technology that allows for the production of ultra-fine particle PEs in hand, we have successfully prepared functionalized PE particles and PE particles with
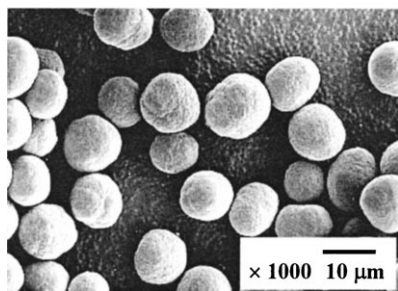

Figure 6. SEM image of the spherical particle PEs produced with MgCl₂-supported Zr-FI catalyst **11**.

polar polymer segments. For example, Zr-FI catalyst **12** (Table 1) (capable of forming vinyl-terminated PEs)[20] supported on ultra-fine particle MgCl₂ converted ethylene to ultra-fine spherical PE particles comprised of vinyl-terminated PE chains (M_n 6600, vinyl 1.34/1000 C). Treatment of these PE particles with m-chloroperbenzoic acid (vinyl conversion 30 %, based on IR analysis) and subsequent reaction of the resultant epoxy-substituted PE particles with amine-terminated polypropylene glycol (H₂N-PPG-NH₂, M_n 2000, purchased from Suntechno Chemicals, Inc.) provided ultra-fine spherical particle PEs with PPG pendants.[12c] The PE–PPG hybrid materials display unique behavior when treated with a decalin/methanol mixture. Namely, the hybrid materials are present in the interface between the methanol and decalin phases, unlike the parent PEs, which exclusively exist in the decalin phase (Figure 7), suggesting that the materials possess the hybrid character of PE and PPG. Structure-wise, the hybrid materials are sorts of dendrimers.
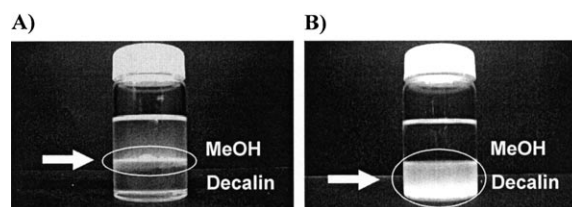

Figure 7. Behavior of ultra-fine particle PEs with and without PPG pendants (A and B, respectively) in the decalin/MeOH biphase mixture.

V-FI catalysts with MgCl₂/Et$_n$Al(OR)$_{3-n}$: In contrast to Group 4 metal-based catalysts, highly active, long-lived V-based catalysts are scant, despite the practical importance of V-based catalysts (e.g., combination of VOCl₃ or V(acac)₃ with alkylaluminum) in the production of ethylene/propylene copolymers and ethylene/propylene/diene elastomers (EPDM). This inactivity is associated with catalyst deactivation typically by means of ligand migration and reduction of the V metal (typically V^{II}), which is induced by the alkylaluminum species. In particular, at technically useful process temperatures, this catalyst decomposition is more pronounced. Consequently, the development of V-based catalysts that demonstrate high productivity at elevated temperatures is an extremely desirable industrial goal in the field of polymerization catalysis.[21]

As stated previously, Ti- and Zr-FI catalysts in combination with MgCl₂-based compounds resulted in highly active MgCl₂-supported catalysts, probably due to the electronic interaction between the catalytically active species and MgCl₂. Bearing this in mind, MgCl₂-supported V-FI catalysts, if developed, may be thermally robust catalysts because the immobilization of a V-FI catalyst onto an MgCl₂ surface through the electronic interaction is likely to mitigate the ligand migration, which presumably retards the reduction of the V metal center.

V-FI catalyst **13** combined with $MgCl_2/Et_nAl(OR)_{3-n}$ was examined as an ethylene polymerization catalyst,[13b, 22] by varying the polymerization temperature (25–75°C) in the presence of Et_2AlCl and ethyl trichloroacetate.[23] The relevant results are summarized in Table 5. For comparison, the polymerization results with V-FI catalyst **13** in the absence of $MgCl_2/Et_nAl(OR)_{3-n}$ and with $VOCl_3/MgCl_2/Et_nAl(OR)_{3-n}$ are also included in Table 5.

Table 5. Ethylene polymerization results for V-FI catalyst **13** and $VOCl_3$.[a]

	Catalyst	Mg[b] [mmol]	T [°C]	Yield [g]	Activity[c]
1[d]	**13**	0.8	25	4.68	18.7
2[d]	**13**	0.8	50	11.53	46.1
3[d]	**13**	0.8	75	16.28	65.1
4[d]	$VOCl_3$	0.8	25	2.07	8.3
5[d]	$VOCl_3$	0.8	50	1.67	6.7
6[d]	$VOCl_3$	0.8	75	1.34	5.4
7	**13**	0	25	5.00	20.0
8	**13**	0	50	3.32	13.3
9	**13**	0	75	1.23	4.9
10	$VOCl_3$	0	25	3.15	12.6
11	$VOCl_3$	0	50	2.03	8.1
12	$VOCl_3$	0	75	1.39	5.6

[a] Conditions: toluene (400 mL), catalyst (1.0 μmol), Et_2AlCl 0.4 mmol, ethyl trichloroacetate (0.4 mmol), ethylene (0.1 MPa), 15 min. [b] Prepared by the reaction of an $MgCl_2/3(2\text{-ethyl-1-hexanol})$ adduct with Et_3Al. [c] kg PE (mmol metal)$^{-1}$ h^{-1}. [d] $MgCl_2/3(2\text{-ethyl-1-hexanol})$ (0.8 mmol) as $MgCl_2$, Et_3Al (2.4 mmol).

An inspection of the data in Table 5 shows that, unlike V-FI catalyst **13** combined with $Et_nAl(OR)_{3-n}$, this FI catalyst with $MgCl_2/Et_nAl(OR)_{3-n}$ displays a higher activity with increasing polymerization temperature, and demonstrates a very high activity of 65.1 kg PE (mmol metal)$^{-1}$ h^{-1} at 75°C. This is remarkable, since higher activity at elevated temperatures is desirable for the process and economic considerations of V-based catalysts. It should be pointed out that $VOCl_3$ in association with $MgCl_2/Et_nAl(OR)_{3-n}$ generates a catalyst that features poor thermal stability. These results indicate that both the phenoxyimine ligand and the $MgCl_2$-based compound are requirements for achieving an unprecedented V-based olefin polymerization catalyst that exhibits a very high activity at an elevated temperature. Considering that V-based catalysts are normally deactivated through ligand migration and reduction of the V center, the combination of the phenoxyimine ligand and $MgCl_2/Et_nAl(OR)_{3-n}$ stabilizes the V center with respect to ligand migration and V reduction. Additionally, the immobilization onto the $MgCl_2$ presumably impedes bimolecular deactivation of the catalyst.[21f]

The V-FI catalyst system provided PEs with well-defined morphology, suggesting that V-FI catalyst **13** with $MgCl_2/Et_nAl(OR)_{3-n}$ is a $MgCl_2$-supported V catalyst, as expected. The PEs produced with this V catalyst system possess exceptionally high molecular weights ($M_v > 5\,000\,000$) and thus

their molecular weights (M_w and M_n) and molecular-weight distributions (M_w/M_n) could not be analyzed with the usual analytical techniques (GPC). However, PEs with lower molecular weights made in the presence of H_2 as a chain-transfer agent were shown to have narrow molecular-weight distributions (M_w/M_n ca. 2.5), consistent with the operation of a single-site catalyst.

Lifetime studies revealed that V-FI catalyst **13** combined with $MgCl_2/Et_nAl(OR)_{3-n}$ exhibits a very high activity at a high temperature of 75°C and maintains this activity for 60 min at this temperature, as indicated by the linear relationship between the polymer yield and the polymerization time (Figure 8). The $MgCl_2$-supported V-FI catalyst **13** represents the first example of a highly active, long-lived V-based catalyst at technical process temperatures. Accordingly, we have achieved an important goal in the field of V-based olefin polymerization catalysis.
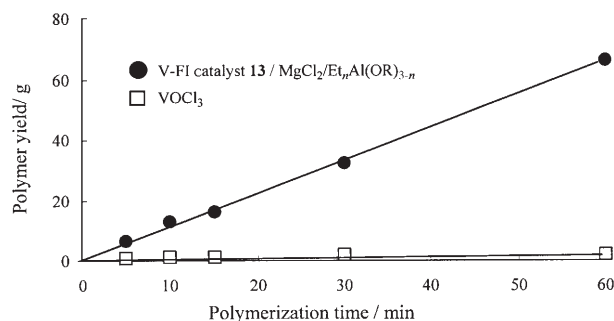

Figure 8. Relationship between the polymerization time and the polymer yield with V-FI catalyst **13**/$MgCl_2/Et_nAl(OR)_{3-n}$ and $VOCl_3$. (Conditions: toluene 400–1600 mL, Et_2AlCl 0.4 mmol, ethyl trichloroacetate 0.4 mmol, ethylene 0.1 MPa, 75°C; (●) V-FI catalyst **13** 1.0 μmol, $MgCl_2/Et_nAl(OR)_{3-n}$ 0.8 mmol as $MgCl_2$; (□) $VOCl_3$ 1.0 μmol).

This thermally robust V catalyst system [**13**/$MgCl_2/Et_nAl(OR)_{3-n}$] was also studied for ethylene/propylene copolymerization at 75°C. The system produced an amorphous copolymer with a propylene content of 21 mol%. The copolymer has a random sequence distribution with a certain amount of propylene inverted units (3%). GPC analysis indicated that the copolymer possesses a very high molecular weight (M_w) of 697000, with a somewhat broadened molecular-weight distribution (M_w/M_n) of 4.72. At this point, it is unclear why this V-FI catalyst system formed a copolymer with a relatively broad molecular-weight distribution unlike the PE with a narrow molecular-weight distribution produced with this catalyst system. Notably, a GPC-IR study demonstrated that the copolymer has a unique comonomer distribution. Thus, the longer copolymer chains possess higher propylene content (Figure 9), which is rather unexpected, but should have beneficial effects on the material properties.
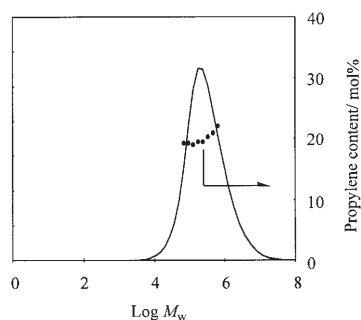
Figure 9. GPC-IR chart of the ethylene–propylene copolymer produced with MgCl$_2$-supported V-FI catalyst **13**.

Application of MgCl$_2$-based Activator/Support for Transition-Metal Complexes with Heteroatom-Containing Ligands other than FI catalysts

We have so far described that combinations of FI catalysts and MgCl$_2$/R$'_n$Al(OR)$_{3-n}$ (R$'$ = Et or *i*Bu, RO = 2-ethyl-1-hexoxy) lead to MAO- and borate-free, high-performance catalysts capable of controlling polymer morphology. Based on our concept regarding the function of MgCl$_2$, we reasoned that MgCl$_2$-based compounds would serve as good activators/supports for transition-metal complexes with heteroatom-containing ligands other than FI catalysts.[13c]

Therefore, we applied MgCl$_2$/R$'_n$Al(OR)$_{3-n}$ as an activator/support to recently-developed heteroatom-based transition-metal complexes for olefin polymerization. The complexes include a pyrrolideimine-ligated Ti complex,[7d, 11a–c] a diimine-ligated Ni complex,[24] and a diiminepyridine-ligated Fe complex.[25] The selected polymerization results are collected in Table 6, which demonstrates the great ability of an MgCl$_2$-based compound to work as an activator for complexes **14–17**.

14 **15**

16 **17**
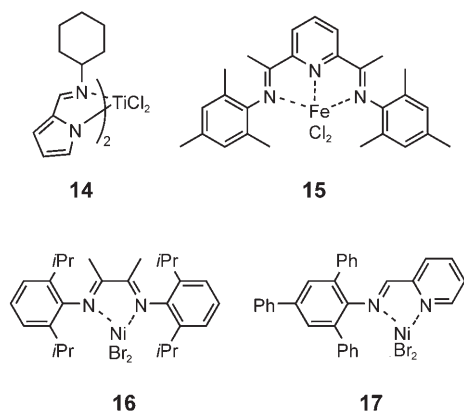
Thus, these heteroatom-based complexes in association with MgCl$_2$/*i*Bu$_n$Al(OR)$_{3-n}$ exhibit high polymerization activities under the given conditions (atmospheric pressure, 25 °C, 30 min). The narrow molecular-weight distributions (M_w/M_n) of 2.05 (**16**) and 2.21 (**17**)[26] revealed the single-site behavior of these catalyst systems. It is noted that complex

Table 6. Ethylene polymerization results for complexes **14–17** with MgCl$_2$/*i*Bu$_n$Al(OR)$_{3-n}$.[a]

	Complex	Yield [g]	Activity[b]	M_w[c] ($\times 10^3$)	M_w/M_n[c]
1	**14**	0.156	0.13	495.0	4.65
2	**15**	1.239	0.99	85.8	2.83
3	**16**	0.763	0.61	319.0	2.05
4	**17**	0.147	0.12	0.4	2.21

[a] Conditions: toluene (250 mL), complex (2.5 μmol), MgCl$_2$/3(2-ethyl-1-hexanol) (1.0 mmol) as MgCl$_2$, *i*Bu$_3$Al (3.0 mmol), ethylene (0.1 MPa), 25 °C, 30 min. [b] kg PE (mmol metal)$^{-1}$ h^{-1}. [c] Determined by GPC using polyethylene calibration.

15 with this MgCl$_2$-based compound forms a PE with a fairly narrow molecular-weight distribution (M_w/M_n 2.83), unlike the corresponding homogeneous counterpart that often produces PEs with broad molecular-weight distributions.[25]

Moreover, like the phenoxy-imine ligated V complex **13** (Table 1), V complexes **18–22**[27] are readily activated and immobilized by an MgCl$_2$-based compound. From Table 7, it
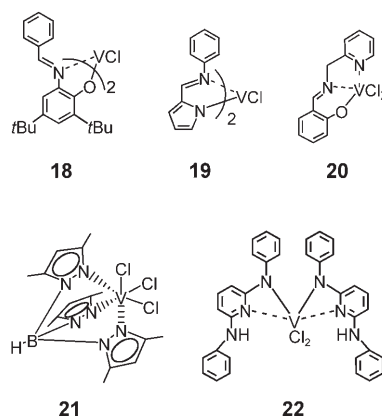

18 **19** **20**

21 **22**

Table 7. Ethylene polymerization results for complexes **18–22** with MgCl$_2$/Et$_n$Al(OR)$_{3-n}$.[a]

	Complex	Yield [g]	Activity[b]	M_v[c] ($\times 10^3$)
1	**18**	15.65	22.8	536
2	**19**	13.61	19.8	423
3	**20**	10.46	15.2	608
4	**21**	15.38	22.4	425
5	**22**	2.16	3.1	509

[a] Conditions: toluene (400 mL), complex (2.75 μmol), MgCl$_2$/3(2-ethyl-1-hexanol) (0.5 mmol) as MgCl$_2$, Et$_3$Al (1.5 mmol), Et$_2$AlCl (0.25 mmol), ethyl trichloroacetate (0.25 mmol), ethylene (0.1 MPa), 75 °C, 15 min. [b] kg PE (mmol metal)$^{-1}$ h^{-1}. [c] Calculated with the following equation: $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$ ($[\eta]$ = intrinsic viscosity, which was measured in decalin at 135 °C).

can be seen that these V complexes with MgCl$_2$/Et$_n$Al(OR)$_{3-n}$ have high activities in the range 3.1–22.8 kg PE (mmol metal)$^{-1}$ h^{-1} at an elevated temperature of 75 °C. These results suggest that highly active V-based catalysts are accessible using combinations of V complexes and MgCl$_2$-based compounds. As anticipated, the PEs arising

from these catalyst combinations (Tables 6 and 7) possess good polymer particle morphology.

It should be emphasized that $MgCl_2/R'_nAl(OR)_{3-n}$ works as a good activator/support for early-to-late transition-metal complexes with various ligand environments. These results show the very high capability of $MgCl_2$-based compounds as activators/supports for transition-metal complexes for olefin polymerization, and at the same time, the results reinforce our concept concerning $MgCl_2$-based compounds as activators/supports described in this article.

Conclusion

We have been able to combine the advantages of homogeneous catalysis with those of heterogeneous catalysis by the combination of transition-metal complexes featuring heteroatom-containing ligands and $MgCl_2$-based compounds. Thus, it is revealed that $MgCl_2/R'_nAl(OR)_{3-n}$ serves as a highly efficient activator/support for recently developed non-metallocene catalysts, which include FI catalysts, Brookhart Ni–diimine catalysts, and Brookhart–Gibson Fe–diiminepyridine catalysts.

The new catalysts discussed herein have achieved some of the long-standing challenges in the field of polymerization catalysis (e.g., MAO- and borate-free, highly active single-site catalysts, $MgCl_2$-supported single-site Ti-based catalysts, and highly active, thermally robust V-based catalysts). Additionally, the development has provided exciting opportunities for the preparation of a number of unique materials, which include highly syndiotactic PPs with exceptionally high T_m's, ethylene/propylene copolymers with peculiar propylene distributions, and PEs with remarkable morphology (e.g., spherical particle PEs with very high molecular weights and with exceptionally high bulk densities, ultra-fine noncoherent spherical particle PEs). These significant results highlight a strategy for developing unique olefin polymerization catalysts by the combination of transition-metal complexes incorporating heteroatom-containing ligands with $MgCl_2$-based compounds.

Given the high catalytic activity and unique catalysis of the new $MgCl_2$-containing transition-metal catalyst systems, it seems likely that new high performance catalysts based on the catalyst combinations introduced herein await discovery.

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