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## *Award Accounts*

**The Chemical Society of Japan Award for Young Chemists in Technical Development for 2002**

# Development of Single-Site New Olefin Polymerization Catalyst Systems Using $MgCl_2$-Based Activators: MAO-Free $MgCl_2$-Supported FI Catalyst Systems

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MAO-free new single-site catalyst systems have been developed for olefin polymerization, which are comprised of bis(phenoxy-imine) Ti, Zr, or V complexes (Ti–, Zr–, or V–FI Catalysts) and $MgCl_2$-based compounds. These new catalyst combinations are highly active single-site (Ti–FI Catalysts), exceptionally active (Zr–FI Catalysts), or highly active, thermally robust, single-site (V–FI Catalyst) catalysts for ethylene polymerization. The catalysts can display higher catalytic performance (i.e., catalytic activity, stereoselectivity, thermal stability) than those activated by the well-established MAO activators. In addition, these catalysts are supported, and thus possess a technological advantage vis-à-vis control over polymer morphology, which is essential for commercial application. Therefore, the application of $MgCl_2$-based compounds capable of working both as an activator and a support for non-metallocene complexes provides a conceptually new strategy for the development of high-performance supported single-site catalysts.

The discovery of highly active olefin polymerization catalysts has been a trigger for creating new polymers which impact our daily lives in countless beneficial ways. The first trigger, in 1953, is Ziegler's discovery of the combination of $TiCl_4$ and alkylaluminum, which displays high ethylene polymerization activity.[1] Followed by Natta's stereoregular propylene polymerization using $TiCl_3$ and alkylaluminum,[2,3] the Ziegler–Natta catalysts resulted in the creation of new polymers such as high-density polyethylene (HDPE) and isotactic polypropylene (iPP). The second trigger, $MgCl_2$-supported Ti catalysts, was discovered independently at Mitsui and at Montecatini in the late 1960s.[4,5] These supported catalysts exhibit an activity two orders of magnitude larger than Ziegler's original catalysts. Kinetic studies have revealed that $MgCl_2$, originally used as a support, functions as a good activator for titanium chloride species.[6] Therefore, this discovery proved that $MgCl_2$ could act as both an activator and a support. These catalysts were used for the commercial production of many high quality, reasonably priced polyolefin products such as linear-low density PE (LLDPE), highly isotactic PP, and polyolefin elastomer.[7] These supported catalysts, however, are multisite catalysts and thus their catalyst design is extremely difficult. Therefore, regarding these supported catalysts, a crucial goal still remaining to be realized is the $MgCl_2$-supported single-site Ti catalysts.[8] In 1980, the third trigger was discovered by Kaminsky, who demonstrated that group 4 metallocenes combined with MAO (methylalmoxane) led to highly active, long-lived, single-site catalysts for ethylene polymerization.[9] This discovery means that MAO is an excellent activator for group 4 metallocenes. Metallocene catalyst systems have created precisely controlled polymers, such as high-performance LLDPE, isotactic and syndiotactic PP, syndiotactic polystyrene (sPS), and so forth, since metallocene catalysts are well-defined transition metal complexes.[10]

Thus, the discovery of highly active catalysts is based on the discovery of highly effective activators, namely $MgCl_2$ for titanium chloride and MAO for metallocenes. Although some attempts have been made to use $MgCl_2$ as an activator for metallocenes,[11] the results have so far not been good. These facts pose a question; why is $MgCl_2$ a far less effective activator for metallocenes than MAO though it works as an excellent activator for titanium chloride species? We have postulated that the high performance of $MgCl_2$ as an activator originates from a direct electronic interaction between the titanium chloride species and $MgCl_2$, presumably through the chloride bound to the Ti and Mg.[20d,52–54] This postulate suggests that $MgCl_2$ does not work as a good activator for metallocenes because of the lack of the direct interaction, and at the same time the postulate indicates that $MgCl_2$ probably functions as a good activator for non-metallocene complexes having heteroatoms in the ligands. If so, based on non-metallocene complexes we can develop $MgCl_2$-supported single-site catalysts, which is a long-standing challenge.

As part of our program to develop high-performance molecular catalysts for olefin polymerization,[12–19] we reported on a new family of bis(phenoxy-imine) early transition metal complexes (named FI Catalysts).[20] FI Catalysts combined with MAO or borate activators[56] display unique polymerization cat-

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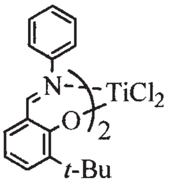
alysis and produce various distinctive polymers with high efficiency.[21–49] For example, FI Catalysts form vinyl-terminated low molecular weight PEs ($M_w$ 1000 to 10000; vinyl selectivity >90%),[23,33] ultra-high molecular weight amorphous ethylene–propylene copolymers ($M_w$ > 10000000),[34] and high tacticity PPs with extremely high peak melting temperatures (sPP: $T_m$ 156 °C, iPP: $T_m$ 165 °C).[20d,32,48] In addition, FI Catalysts can mediate highly controlled living ethylene polymerization and highly syndiospecific living propylene polymerization and can thus create a variety of block copolymers from ethylene and propylene.[20a,25–27,30,32,40] Many of these polymers were unavailable prior to our work. Accordingly, FI Catalysts and related early transition metal complexes have drawn considerable attention as olefin polymerization catalysts in recent years.[50]

Unlike common group 4 metallocenes, FI Catalysts possess O and N heteroatoms in the ligands, which can interact electronically with $MgCl_2$, and thus we expected that $MgCl_2$ would work as an activator for FI Catalysts. Additionally, we felt that $MgCl_2$ would be a very attractive activator candidate because it was originally discovered at Mitsui as a support for $TiCl_4$,[4] and it is white, harmless and cost-competitive. Therefore, we decided to investigate $MgCl_2$ as an activator for FI Catalysts. We hope that this study will give insight into the nature of heterogeneous Ziegler–Natta catalysts as well as provide higher performance FI Catalyst systems.

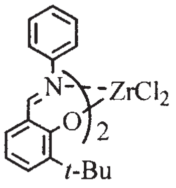
We describe herein new olefin polymerization catalyst systems composed of Zr, Ti, and V-FI Catalysts and $MgCl_2$-based activators, which can be highly active, MAO-free, supported single-site catalysts for olefin polymerization.[51–55]

## 1. Verification of the Hypothesis

In order to verify our hypothesis (i.e., $MgCl_2$ would work as an activator for FI Catalysts), ethylene polymerizations were carried out with Ti–FI Catalyst **1** and Zr–FI Catalyst **7** (Fig. 1) in the presence of mechanically-pulverized $MgCl_2$ (vibromill; 8 h, crystallite size 80 Å)[57] at 50 °C under 0.9 MPa ethylene pressure. $Et_3Al$ was employed as an alkylating agent for the FI Catalysts as well as a scavenger in a polymerization system.



**1**



**7**

Fig. 1. Structures of Ti–FI Catalyst **1** and Zr–FI Catalyst **7**.

The relevant results are collected in Table 1, which also contains the results for **1** and **7** with $Et_3Al$, as a comparison.

The data in Table 1 shows that FI Catalysts **1** and **7** with $Et_3Al/MgCl_2$ catalyzed the polymerization of ethylene to produce high molecular weight PEs [viscosity-average molecular weights ($M_v$), **1**: 2430000, **7**: 710000]. In contrast, these FI Catalysts with $Et_3Al$ displayed virtually no reactivity towards ethylene, generating neither polymeric nor oligomeric materials. These results indicate that $MgCl_2$ can activate FI Catalysts for the polymerization of ethylene. The catalytic activities obtained with the FI Catalysts in combination with $Et_3Al/MgCl_2$ (0.3 and 3.4 kg-PE/mmol-cat/h) are very high for a MAO-free catalyst system. The $MgCl_2$ employed presumably functions as a Lewis acid to form a cationic active species from the ethylated FI Catalysts and becomes an anionic species which works as a counter anion to the cationic active species.[58]

It should be pointed out that $[Cp_2TiCl_2]$ or $[Cp_2ZrCl_2]$ with $Et_3Al/MgCl_2$ was a poor catalyst and provided only a trace amount of PE (<0.1 kg-PE/mmol-cat/h) under identical conditions. Based on the above results, we concluded that $MgCl_2$ possesses a good potential as an activator for FI Catalysts and that a direct electronic interaction between the cationic active species derived from FI Catalysts and $MgCl_2$ (probably through the O and N heteroatoms in the ligand and Mg) may be responsible for the high activities obtained.[52–54] The direct interaction between the O and N in the ligand and Mg might assist the electron transfer between the ligand and the metal, reducing the barrier to ethylene insertion. In this regard, one can say that $MgCl_2$ plays a role as a ligand though it interacts indirectly with the metal center.

## 2. Catalytic Performance of FI Catalysts in the Presence of $MgCl_2$-Based Compounds

**2.1 Ti–FI Catalysts with $MgCl_2$-Based Activator Systems.** The $MgCl_2$-based activator used for Ti–FI Catalysts, $MgCl_2/i\text{-}Bu_mAl(OR)_n$, was prepared by the de-alcoholysis of a $MgCl_2$/2-ethyl-1-hexanol adduct with $i\text{-}Bu_3Al$, since this method produces highly porous and finely dispersed $MgCl_2$, which should be a more suitable activator for FI Catalysts than mechanically-pulverized $MgCl_2$. X-ray analysis indicated the formation of $MgCl_2$ having a crystallite size of 28 Å determined by the (110) reflection.[57] Olefin polymerizations with Ti–FI Catalysts were conducted using the resulting $MgCl_2/i\text{-}Bu_mAl(OR)_n$ as an activator. We believe that the resulting aluminum species, such as $i\text{-}Bu_2Al$(2-ethyl-1-hexoxide), would work as in situ alkylating reagents for Ti–FI Catalysts as well as scavengers in a polymerization system, similar to the $Et_3Al$ in the FI Catalysts **1** and **7** with $Et_3Al/MgCl_2$ systems discussed above.

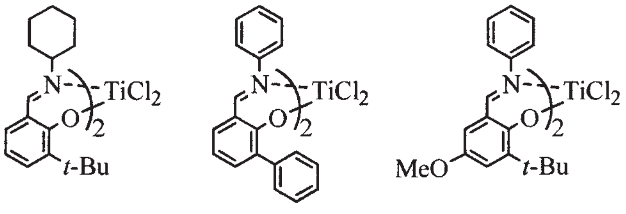
Table 1. Ethylene Polymerization Results with FI Catalysts **1** and **7**/$Et_3Al$ with and without $MgCl_2$[a)]

| Entry | Catalyst /μmol | $MgCl_2$ /mmol | $Et_3Al$ /mmol | Yield /g | Activity[b)] | $M_v$ /×$10^{-4}$ |
|---|---|---|---|---|---|---|
| 1[c)] | **1** (2.0) | 0.4 | 0.4 | 0.32 | 0.3 | 243 |
| 2[c)] | **1** (2.0) | 0 | 0.4 | trace | — | — |
| 3[d)] | **7** (8.0) | 1.6 | 0.2 | 9.10 | 3.4 | 70.6 |
| 4[d)] | **7** (8.0) | 0 | 0.2 | trace | — | — |

a) Conditions: 50 °C, 0.9 MPa ethylene pressure; solvent, toluene 500 mL. b) Activity: kg of polymer/mmol of cat/h. c) Polymerization time, 30 min. d) Polymerization time, 20 min.

Ethylene polymerizations with Ti–FI Catalysts **1**–**4** (Fig. 2) were carried out using $MgCl_2/i\text{-}Bu_mAl(OR)_n$ as an activator under 0.9 MPa ethylene pressure for 30 min at 50 °C. The polymerization results are collected in Table 2, which also includes the results obtained with the FI Catalysts with MAO activation, as a comparison.

As anticipated, Ti–FI Catalysts **1**–**4** with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activation are highly active catalysts for ethylene polymerization, though these FI Catalysts combined with $i\text{-}Bu_mAl(OR)_n$ or $i\text{-}Bu_3Al$ are poor catalysts for the polymerization. The activities seen with the $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activation systems (20.8–36.0 kg-PE/mmol-cat/h) are very high for a Ti-based catalyst and, in fact, they are comparable to or exceeding that obtained with the $[Cp_2TiCl_2]$/MAO catalyst system under the same reaction conditions. It is of great significance that the activities obtained with the $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activators are comparable to those seen with the well-established MAO activator systems. These results further confirmed the high potential of $MgCl_2$ as an activator for FI Catalysts.



**2** **3** **4**

Fig. 2. Structures of Ti–FI Catalysts **2**–**4**.

Significantly, the PEs formed with the Ti–FI Catalysts/$MgCl_2/i\text{-}Bu_mAl(OR)_n$ systems show the morphology of well-defined particles [Fig. 3(a)]. On the other hand, the PEs produced with the MAO activation systems display ill-defined polymer morphology [Fig. 3(b)]. These facts suggest that the FI Catalysts exist on the surface of the solid $MgCl_2/i\text{-}Bu_mAl(OR)_n$ activator and that the polymerization occurred on the surface. Thus, the Ti–FI Catalysts with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ systems were demonstrated to be $MgCl_2$-supported catalyst systems. The direct interaction between the O and N in the ligands and Mg as well as the electrostatic interaction between the cationic active species and the anionic activator probably accounts for the formation of the $MgCl_2$-supported catalysts.

Notably, the Ti–FI Catalysts **1**–**3**/$MgCl_2/i\text{-}Bu_mAl(OR)_n$ systems furnished narrow molecular weight distribution PEs ($M_w/M_n$ 2.40–2.67; MAO activation $M_w/M_n$ 2.07–2.74) though the Ti–FI Catalyst **4** system provided a relatively broad molecular weight distribution PE ($M_w/M_n$ 3.51; MAO activation: $M_w/M_n$ 4.74) (Table 2). These results show that the $MgCl_2$-supported Ti–FI Catalysts can work as single-site catalysts, representing the first examples of single-site catalysts

Table 2. Ethylene Polymerization Results with Ti–FI Catalysts **1**–**4** Combined with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ or MAO as an Activator$^{a)}$

| | | | Amount of activator | | Yield | | $M_w$$^{c)}$ | |
|---|---|---|---|---|---|---|---|---|
| Entry | Catalyst | Activator | Mg/mmol | Al/mmol | /g | Activity$^{b)}$ | $/\times10^{-4}$ | $M_w/M_n$$^{c)}$ |
| 1 | **1** | $MgCl_2/i\text{-}Bu_mAl(OR)_n$ | 0.40 | 2.40 | 9.07 | 36.3 | 50.9 | 2.66 |
| 2 | **2** | $MgCl_2/i\text{-}Bu_mAl(OR)_n$ | 0.40 | 2.40 | 5.21 | 20.8 | 59.6 | 2.67 |
| 3 | **3** | $MgCl_2/i\text{-}Bu_mAl(OR)_n$ | 0.40 | 2.40 | 9.01 | 36.0 | 23.1 | 2.40 |
| 4 | **4** | $MgCl_2/i\text{-}Bu_mAl(OR)_n$ | 0.40 | 2.40 | 6.54 | 26.2 | 117 | 3.51 |
| 5 | **1** | MAO | 0 | 1.25 | 11.16 | 44.6 | 46.4 | 2.38 |
| 6 | **2** | MAO | 0 | 1.25 | 5.35 | 21.4 | 62.5 | 2.74 |
| 7 | **3** | MAO | 0 | 1.25 | 24.77 | 99.1 | 22.9 | 2.07 |
| 8 | **4** | MAO | 0 | 1.25 | 17.01 | 68.0 | 42.2 | 4.74 |

a) Conditions: 50 °C, 0.9 MPa ethylene pressure; solvent, toluene 500 mL; polymerization time, 30 min; **1**–**4** 0.5 µmol. b) Activity: kg of polymer/mmol of cat/h. c) Determined by GPC.

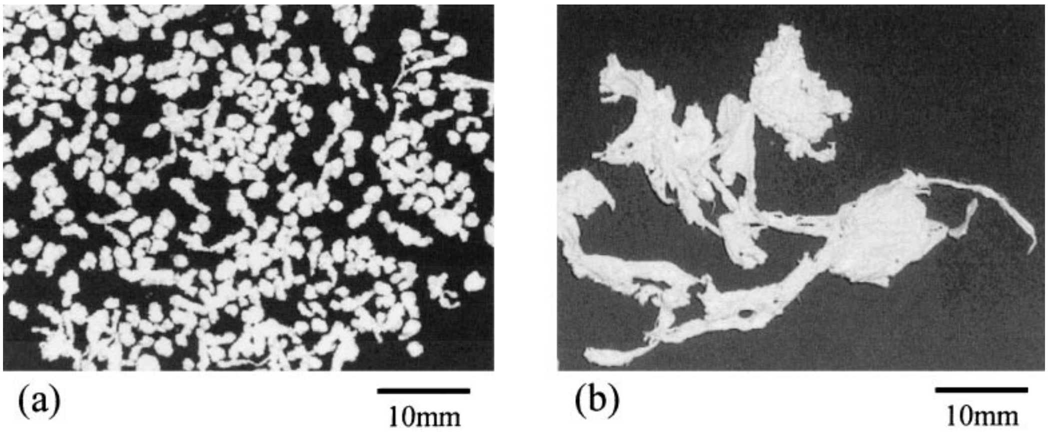


Fig. 3. Photographs of the PEs formed with **1** using (a) $MgCl_2/i\text{-}Bu_mAl(OR)_n$ or (b) MAO as an activator.

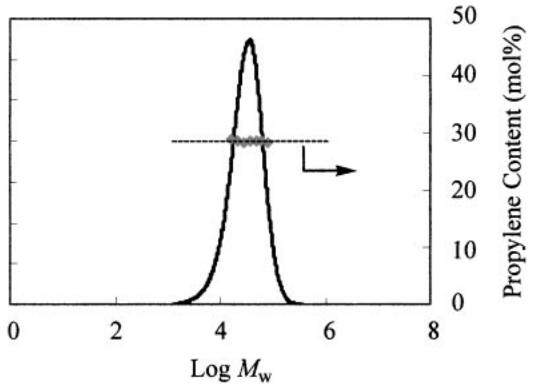
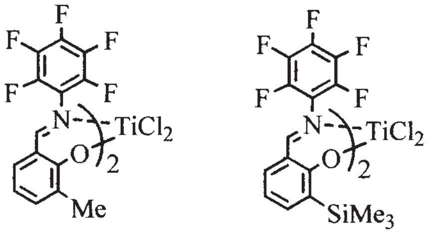


Fig. 4. GPC–IR chart of the ethylene–propylene copolymer arising from Ti–FI Catalyst **3**/$MgCl_2$/*i*-$Bu_mAl(OR)_n$.



**5** **6**

Fig. 5. Structures of Ti–FI Catalysts **5** and **6**.

based on non-metallocene complexes and $MgCl_2$-based activators. Therefore, we have developed MAO-free, $MgCl_2$-supported single-site catalysts based on Ti–FI Catalysts and $MgCl_2$-based activators, which was the long-standing challenge in the field of olefin polymerization catalysis.

To further confirm the single-site catalysis of the Ti–FI Catalyst systems, ethylene/propylene copolymerization using Ti–FI Catalyst **3** with $MgCl_2$/*i*-$Bu_mAl(OR)_n$ was performed. The system produced an amorphous copolymer having a propylene content of 29 mol% (IR analysis) with a molecular weight distribution of 1.70, exhibiting a high activity of 28 kg-polymer/mmol-cat/h. GPC–IR analysis indicated the uniform incorporation of propylene (Fig. 4).

These results clearly reflect the single-site nature of the $MgCl_2$-supported Ti–FI Catalyst and its ability to form copolymers with a uniform comonomer distribution. Thus, $MgCl_2$-supported Ti–FI Catalysts can combine high catalytic activities with the generation of (co)polymers having narrow molecular weight distributions and homogeneous structures.[52]

As an application, $MgCl_2$/*i*-$Bu_mAl(OR)_n$ was investigated as an activator for living Ti–FI Catalyst **5** (Fig. 5) capable of inducing living propylene polymerization upon activation with MAO.[40] The catalyst system polymerized propylene in a living fashion and produced a narrow molecular weight distribution PP ($M_w/M_n$ 1.09, $M_n$ 53000; 25 °C, atmospheric pressure, 1 h).[55] The living nature was confirmed by the linear relationship between $M_n$ and polymerization time as well as by the narrow $M_w/M_n$ values observed (Fig. 6). This is the first example of living propylene polymerization promoted by a MAO- and borate-free Ti catalyst system.[59]

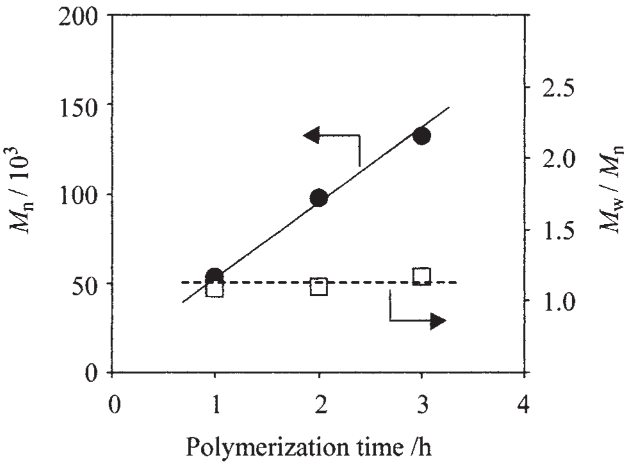
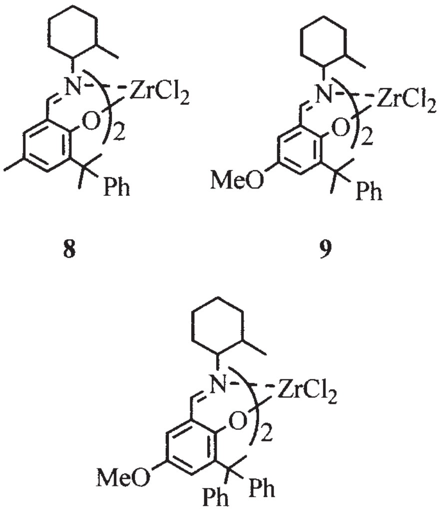


Fig. 6. Plots of $M_n$ and $M_w/M_n$ as a function of polymerization time for propylene polymerization with **5**/$MgCl_2$/*i*-$Bu_mAl(OR)_n$. Conditions: 0.1 MPa propylene pressure; solvent, toluene 250 mL; polymerization temperature, 25 °C; **5** 20 μmol, $MgCl_2$/$Et_mAl(OR)_n$ 4.0 mmol-Mg (12.0 mmol-Al).



**8** **9**

**10**

Fig. 7. Structures of Zr–FI Catalysts **8**–**10**.

To our surprise, at 25 °C the Ti–FI Catalyst **6** (Fig. 5)[32,40] in combination with $MgCl_2$/*i*-$Bu_mAl(OR)_n$ produced highly syndiotactic PP with an exceptionally high peak melting temperature ([rr] 97%, $T_m$ 155 °C).[55] The $T_m$ value of 155 °C represents the highest for sPPs synthesized at room temperature. This is the first example of highly syndiotactic PP produced with $MgCl_2$-supported Ti catalysts. It is interesting to note that the stereoselectivity and $T_m$ obtained with the $MgCl_2$/*i*-$Bu_mAl(OR)_n$ activation system are higher than those seen with the MAO activation system ([rr] 93%, $T_m$ 152 °C).[32,40] These facts demonstrate that $MgCl_2$-based compounds can be a remarkable activator for olefin polymerization.

**2.2. Zr–FI Catalysts with $MgCl_2$-Based Activator Systems.** $MgCl_2$/*i*-$Bu_mAl(OR)_n$ also worked as an excellent activator for Zr–FI Catalysts for the polymerization of ethylene. Thus, Zr–FI Catalysts **7**–**10** (Fig. 7) combined with $MgCl_2$/*i*-$Bu_mAl(OR)_n$ converted ethylene to PEs with high productivity.[54] The catalytic activities exhibited by the Zr–FI Catalysts/

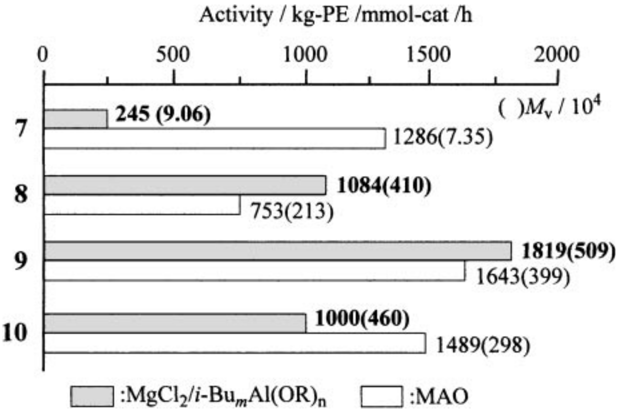


Fig. 8. Ethylene polymerization results of Zr–FI Catalysts **7**–**10** with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ or MAO as an activator. Conditions: 50 °C, 0.9 MPa ethylene pressure; solvent, toluene 500 mL; polymerization time, 30 min; **7**–**10** 0.016 µmol, $MgCl_2/i\text{-}Bu_mAl(OR)_n$ 0.2 mmol-Mg (0.8 mmol-Al).

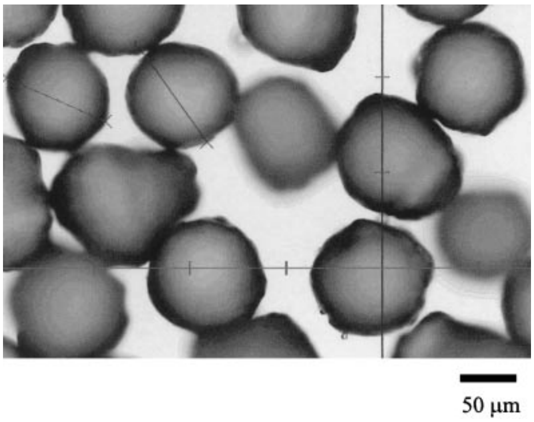


Fig. 9. PEs formed with a Zr–FI Catalyst with $MgCl_2$-based activator system.

$MgCl_2/i\text{-}Bu_mAl(OR)_n$ systems were in the range of 245–1819 kg-PE/mmol-cat/h (Fig. 8), which are some of the highest values for ethylene polymerization catalysts known. Notably, the activities for Zr–FI Catalysts **7** and **8** with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ exceed those for the MAO activator systems.

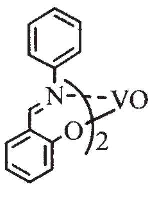
As expected, the PEs produced with the Zr–FI Catalysts **7**–**10**/$MgCl_2$-based activator systems displayed well-defined particles, confirming that these systems are also $MgCl_2$-supported catalysts. Since the morphology of the polymer particle can be controlled by the form of the employed support,[60,61] the systems have the possibility of controlling the polymer morphology. In fact, a Zr–FI Catalyst with $MgCl_2$-based activator system produced very high molecular weight PEs ($M_v$ 3000000; 80 °C, 0.9 MPa ethylene pressure) with an exceptionally high bulk density value of 0.47 g/mL (Fig. 9),[55] which is one of the highest bulk density values ever achieved for PEs. These results indicate the remarkably high potential of Zr–FI Catalysts with $MgCl_2$-based activator systems as supported catalysts.

The PEs formed from Zr–FI Catalyst **7** with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ possess a broad molecular weight distribution ($M_w/M_n$ 13.16, $M_w$ 51300), suggesting that several active species are generated in this catalytic system. Considering that an FI Catalyst can display more than one catalytically active species arising from the coordination modes of two non-symmetric phenoxy-imine ligands in an octahedral geometry, the formation of the broad molecular weight distribution PEs with the Zr–FI Catalyst **7** system is not surprising. We often observe multimodal behavior of FI Catalysts/MAO systems[37,39,49] and, in fact, **7** with MAO produced broad molecular weight distribution PEs ($M_w/M_n$ 13.36, $M_w$ 71000) under identical polymerization conditions. We were not able to determine the molecular weight distributions ($M_w/M_n$) of the PEs produced by the Zr–FI Catalysts **8**–**10** systems due to their exceptionally high molecular weights ($M_v > 40000000$), which represent some of the highest values among PEs produced with complex catalysts.

**2.3. V–FI Catalyst with $MgCl_2$-Based Activator System.** V-based olefin polymerization catalysts represented by $VOCl_3$ and $[V(acac)_3]$ with alkylaluminum compounds are useful single-site catalysts, and are widely used for the industrial production of ethylene/propylene/diene elastomers (EPDM).[62] Although these catalysts display a number of favorable performance characteristics as single-site catalysts, they have a serious drawback; namely, V-based catalysts exhibit low productivity at high process temperatures because of catalyst deactivation caused by the thermal instability of active species. Consequently, the development of thermally stable V-based catalysts is an extremely desirable industrial goal.[63] In general, catalyst deactivation processes include reduction of the V metal [typically to V(II)] and ligand migration.

As described, Ti– and Zr–FI Catalysts combined with $MgCl_2$-based compounds resulted in $MgCl_2$-supported catalysts, probably due to the electronic interaction between the O and N heteroatoms in the ligand and Mg. With a knowledge of these facts, $MgCl_2$-supported V–FI Catalysts, if developed, are expected to be thermally robust catalysts since the fixation of a V–FI Catalyst onto $MgCl_2$ surface through the direct electronic interaction between a catalyst and $MgCl_2$ probably suppresses the ligand migration, which should lead to mitigating the reduction of the V metal center.

V–FI Catalyst **11** (Fig. 10)[64] in association with $MgCl_2/Et_mAl(OR)_n$ was examined as an ethylene polymerization catalyst, varying the polymerization temperatures (25–75 °C) in the presence of $Et_2AlCl$ and ethyl trichloroacetate (ETA).[65] The $MgCl_2$ employed for the V–FI Catalyst, $MgCl_2/Et_mAl(OR)_n$, was synthesized by the de-alcoholysis of a $MgCl_2$/2-ethyl-1-hexanol adduct with $Et_3Al$, using a procedure similar to that used for the de-alcoholysis with $i\text{-}Bu_3Al$. The polymerization results are shown in Fig. 11. As can be seen from Fig. 11, increasing the polymerization temperature afforded a correspond-



**11**

Fig. 10. Structure of V–FI Catalyst **11**.

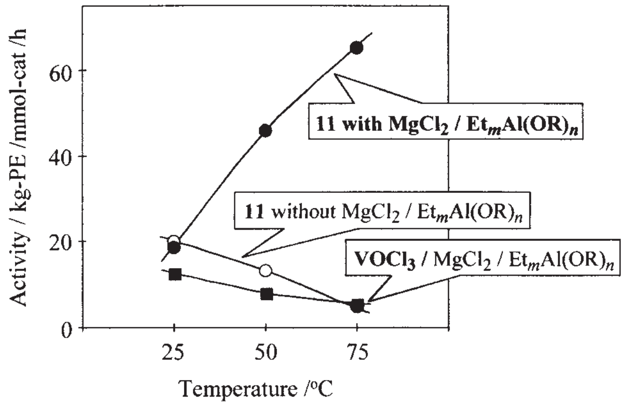


Fig. 11. Relationship between the polymerization temperature and the polymerization activity obtained with V–FI Catalyst **11** and **$VOCl_3$** in the presence or absence of $MgCl_2/Et_mAl(OR)_n$. Conditions: 0.1 MPa ethylene pressure; solvent, toluene 400 mL; polymerization time, 15 min; **11** or **$VOCl_3$** 1.0 μmol, $MgCl_2/Et_mAl(OR)_n$ 0.8 mmol-Mg (2.40 mmol-Al), $Et_2AlCl$ 0.4 mmol, ETA 0.4 mmol.

ing increase in activity, though V–FI Catalyst **11** without $MgCl_2$ behaved as a poor catalyst. Interestingly, $VOCl_3$ with $MgCl_2/Et_mAl(OR)_n$ is a catalyst with poor thermal stability. These results indicate that the combination of the phenoxy-imine ligand and a $MgCl_2$-based compound results in the unprecedented V-based olefin polymerization catalyst. The V–FI Catalyst **11**/$MgCl_2/Et_mAl(OR)_n$ system provided PEs with well-defined morphology, suggesting that the resultant catalyst is a $MgCl_2$-supported V catalyst, as expected. While the PEs produced with the **11**/$MgCl_2/Et_mAl(OR)_n$ system possess exceptionally high molecular weights ($M_v > 5000000$) for which we are unable to determine molecular weights ($M_n$) and molecular weight distributions ($M_w/M_n$) using GPC analysis, the PEs produced in the presence of hydrogen as a chain transfer agent have narrow molecular weight distributions ($M_w/M_n$ ca. 2.5). These results demonstrate that the $MgCl_2$-supported V–FI Catalyst **11** is a single-site catalyst.

The productivity of V–FI Catalyst **11** with $MgCl_2/Et_mAl(OR)_n$ was examined at 75 °C over 5–60 min polymerization time under atmospheric pressure (Fig. 12). The polymer yield was revealed to increase linearly with the polymerization time, indicating that the catalyst deactivation is negligible even at 75 °C and at atmospheric pressure for 60 min for the V–FI Catalyst **11** system. By contrast, the $VOCl_3$ catalyst system decayed rapidly and became virtually inactive after ca. 15 min (Fig. 12).

The V–FI Catalyst **11**/$MgCl_2/Et_mAl(OR)_n$ system represents the first example of a highly-active, thermally robust, long-lived V-based catalyst at technically useful process temperatures. Therefore, we have achieved the crucial goal in the field of V-based olefin polymerization catalysis, which is the development of thermally stable V catalysts. Considering that V catalysts are normally deactivated through the reduction of the V center and ligand migration, the combination of the phenoxy-imine ligand and $MgCl_2/Et_mAl(OR)_n$ stabilizes the V center towards reduction and impedes ligand migration, which enables the formation of the thermally stable V catalyst.[53,54]

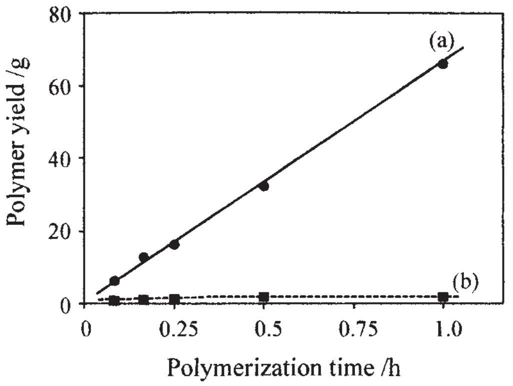


Fig. 12. Relationship between the polymerization time and the polymer yield obtained with V–FI Catalyst **11**/$MgCl_2/Et_mAl(OR)_n$ and $VOCl_3$. Conditions: 75 °C, 0.1 MPa ethylene pressure; solvent, toluene 400–1600 mL; (a) **11** 1.0 μmol, $MgCl_2/Et_mAl(OR)_n$ 0.8 mmol (Mg), $Et_2AlCl$ 0.4 mmol, ETA 0.4 mmol; (b) $VOCl_3$ 1.0 μmol, $Et_2AlCl$ 0.4 mmol, ETA 0.4 mmol.

## 3. Application of $MgCl_2$-Based Activators for Non-Metallocene Complexes

The high performance of $MgCl_2$-based compounds as activators for FI Catalysts has been discussed. Based on the results described herein, the high catalytic properties of the FI Catalysts/$MgCl_2$-based activator systems are thought to originate from the direct electronic interaction between the O and N heteroatoms in the phenoxy-imine ligands and Mg of $MgCl_2$. Hence, $MgCl_2$-based compounds are expected to function as good activators for transition metal complexes possessing heteroatom(s) in the ligand (non-metallocene complexes).[66] In fact, non-metallocene complexes such as **12–16** (Fig. 13)[13,14,17,18,67–69] can be highly active supported ethylene polymerization catalysts in combination with $MgCl_2$-based compounds.[55] These results suggest that $MgCl_2$-based compounds have significant potential as activators and as supports for non-metallocene complexes for olefin polymerization. The development of high-performance supported olefin polymerization catalysts based on non-metallocene complexes other than FI Catalysts and $MgCl_2$-based activators await discovery.

## 4. Conclusion

In summary, MAO-free new supported olefin polymerization catalyst systems have been developed, which are based on bis(phenoxy-imine) Ti, Zr, or V complexes (Ti–, Zr–, or V–FI Catalysts) combined with $MgCl_2$-based compounds. These new catalyst combinations can be highly active single-site catalysts which often display higher activities than the corresponding MAO activation systems, and display higher catalytic properties (e.g., stereoselectivity, thermal stability) than those activated with MAO. Moreover, our new $MgCl_2$-supported catalysts are capable of producing polymers with good morphology (e.g., PE bulk density 0.47 g/mL). The $MgCl_2$-based activators that we developed can activate non-metallocene complexes aside from FI Catalysts to form high-activity supported catalysts for ethylene polymerization. These results indicate the exceptional potential of $MgCl_2$-based compounds

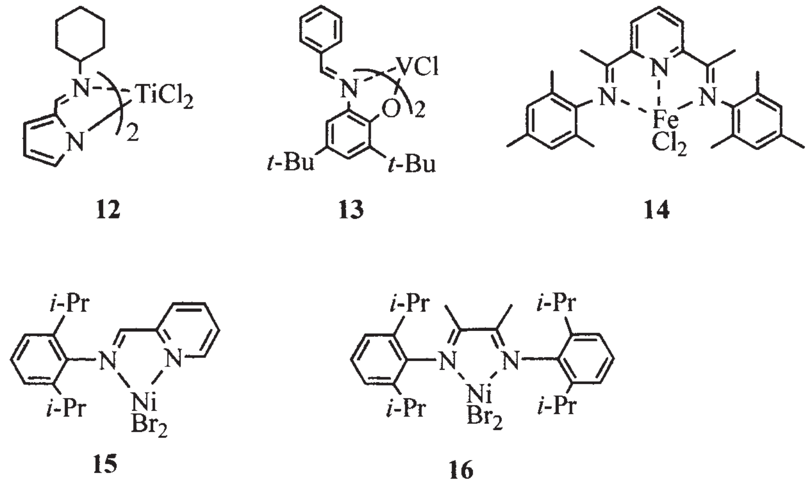


Fig. 13. Non-metallocene complexes **12–16** displaying high ethylene polymerization activities in combination with MgCl$_2$-based activators.

as activators and as supports for transition metal complexes with heteroatom(s) in the ligand. We hope that the results introduced herein will promote research on MgCl$_2$-based activators for olefin polymerization catalysts, which will result in the development of additional high-performance single-site olefin polymerization catalysts.

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