Propylene Polymerization by Using TiCl$_4$ Catalyst Supported on Solvent-Activated Mg(OEt)$_2$

KAP KU KANG,[1] KWANG-SOO KIM,[2] DONG-HO LEE,[3] YOUNG-TAE JEONG[4]

[1] R & D Center, Korea Petrochemical Industries Company, Ltd., 178 Bukok-dong, Nam-ku, Ulsan 680-110, South Korea

[2] Polyolefins Production Team, Technical Group, SK Corporation, Ulsan 680-130, South Korea

[3] Department of Polymer Science, Kyungpook National University, Taegu 702-701, South Korea

[4] Department of Chemistry, Pusan National University, Pusan 609-735, South Korea

ABSTRACT: Solvent activation of Mg(OEt)$_2$ in ethanol with carbon dioxide was carried out in a 1-L three-neck flask under nitrogen atmosphere, to investigate structural changes of Mg(OEt)$_2$ support. During activation of Mg(OEt)$_2$ by ethanol and CO$_2$, a suspension mixture was converted to a clear solution and CO$_2$ was inserted into the Mg—O bond of Mg(OEt)$_2$, to form magnesium ethyl carbonate. The solid supports were obtained from the removal of solvents by heating, during which CO$_2$ split off from the magnesium ethyl carbonate between 100 and 150°C. The structural changes of the obtained supports and the corresponding catalysts were checked by IR and TGA. The polymerization behavior of propylene with the catalyst and morphology of the obtained polymer were also examined. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 460–467, 2001

Key words: catalyst; magnesium ethyl carbonate; polymerization; solvent activation; support

INTRODUCTION

The preparation and characterization of MgCl$_2$-supported highly active titanium catalyst have been studied intensively.[1] However, the use of MgCl$_2$ itself as a catalyst support is not practical because the MgCl$_2$-supported catalysts have high chlorine content and handling MgCl$_2$ is not easy because of its high hygroscopicity. For these reasons, magnesium alkoxides were used and reported as effective supports in some patents.[2,3] However, there are only a few systematic studies on the Mg(OR)$_2$-supported titanium catalysts for olefin polymerization.[4,5]

Recently, we studied in detail the preparation, chemical composition, and characterization of Mg(OEt)$_2$-supported TiCl$_4$ catalysts for the synthesis of isotactic polypropylene.[6–12] However, these catalysts still have problems concerning morphology control of catalysts, such as particle size, particle size distribution, and particle shape. As an approach to overcome the problems, Mg(OEt)$_2$ support was modified by the solvation method, using some reagents[13] to obtain a morphologically uniform catalyst and polymer. To date, however, systematic studies on this modification of Mg(OEt)$_2$ support for propylene catalyst have not been reported.

In this study, we report in detail on the preparation and structural changes of not only Mg(OEt)$_2$ support activated by solvation with eth-

anol and carbon dioxide but also the resulting catalysts for propylene polymerization.

EXPERIMENTAL

Materials

Propylene (purity > 99.5%; Korea Petrochemical Ind. Co.) and carbon dioxide (99.99%) were used without further purification. Nitrogen of an extra pure grade (99.999%) and n-hexane were dried by being passed through molecular sieve columns of 3 and 4 Å, respectively. Toluene was refluxed for 24 h over metallic sodium and distilled under nitrogen atmosphere. Magnesium ethoxide [Mg(OEt)$_2$; Dynamit Nobel Chemie] was used after vibration milling under nitrogen atmosphere for 6 h at room temperature. Ethyl benzoate (EB; Junsei Chemical Co.), benzoyl chloride (BC; Junsei Chemical Co.), anhydrous ethanol (Hayman Limited), triethylaluminum (TEA; Tosoh Akzo Corp.), and titanium tetrachloride (Toho Titanium Co.) were used without further purification.

Activation of Supports

Support 1

A mixture of 10 g (87.4 mmol) of Mg(OEt)$_2$ and 100 mL of ethanol was stirred to form a suspension in a 1-L three-neck flask, equipped with a magnetic stirrer and a condenser under nitrogen atmosphere. The suspension was directly brought into contact with CO$_2$ gas at room temperature until it became a clear solution. The clear mixture was heated to 90°C, at which temperature it was kept for 6 h to remove ethanol. The resulting solid was washed several times with 300 mL of n-hexane and dried under vacuum.

Support 2

Support **1** obtained was heated at 150°C for 2 h and then washed several times with 300 mL of n-hexane and dried under vacuum.

Support 3

The experiments were carried out in the same manner as described under Support **1,** except that a mixture of ethanol (50 mL) and xylene (50 mL) was used instead of ethanol (100 mL) for a suspension, and the removal of solvents was performed at 180°C for 8 h instead of at 100°C for 6 h.

Preparation of Catalysts

Catalyst 1[7]

In a 500-mL four-neck flask, equipped with a magnetic stirrer and a condenser, 80 mL of toluene and 1.0 g (8.74 mmol) of ball-milled Mg(OEt)$_2$ were added under nitrogen atmosphere and stirred to form a suspension. TiCl$_4$ [7.5 mL (68.2 mmol)] was added to the suspension, after which the reaction mixture was allowed to react at 110°C for 2 h. After cooling, the solid product was separated, washed several times with 200 mL of n-hexane to remove unreacted TiCl$_4$, and dried under vacuum.

Catalyst 2

In the same procedure as described under Support **1,** the suspension mixture of Mg(OEt)$_2$ (1 g) and ethanol (10 mL) was directly brought into contact with CO$_2$ gas to obtain a clear solution. TiCl$_4$ (7.5 mL) was directly dropped into the resultant solution. The precipitated solid was separated, washed several times with 200 mL of n-hexane, and dried under vacuum.

Catalyst 3

The experiments were carried out in the same manner as described under Catalyst **1,** except that 1 g of support **1** was used instead of ball-milled Mg(OEt)$_2$.

Catalyst 3*

Catalyst 3 obtained was retreated with TiCl$_4$ (7.5 mL) in the presence of toluene (80 mL) at 110°C for 2 h.

Catalyst 4

The experiments were carried out in the same manner as described under Catalyst **1,** except that 1 g of support **2** was used instead of ball-milled Mg(OEt)$_2$.

Catalyst 4*

Catalyst 4 obtained was retreated with TiCl$_4$ (7.5 mL) in the presence of toluene (80 mL) at 110°C for 2 h.

Catalyst 5

The experiments were carried out in the same manner as described under Catalyst **1,** except

that 1 g of support **3** was used instead of ball-milled $Mg(OEt)_2$.

Catalyst 6

The experiments were carried out in the same manner as described under Catalyst **4,** except that EB (1.3 mmol) as internal donor was added at 110°C after treatment of $TiCl_4$.

Catalyst 7

The experiments were carried out in the same manner as described under Catalyst **6,** except that BC (1.3 mmol) was used instead of EB.

Polymerization and Isotactic Index of Polymer

Propylene polymerization was conducted in a 200-mL glass reactor equipped with a magnetic stirrer. After measured amounts of n-hexane, tri-ethylaluminum, and external donor (if necessary) were added to the reactor under nitrogen atmosphere, propylene was introduced at the polymerization temperature until the solvent was saturated with propylene. Polymerization was started by adding the catalyst to the reactor and performed at 50°C for 2 h. The polymerization was terminated by addition of a dilute solution of hydrochloric acid in ethanol. The precipitated polymers were filtered out, washed with plenty of ethanol, and dried under vacuum at 60°C for 8 h. The isotactic index[6,10,12] of the obtained polymers was determined by extraction with boiling heptane for 6 h.

Analytical Procedure

Analyses of the catalysts and polymers obtained were performed according to previously published methods.[6,10,12] The Ti contents of the catalysts were measured by an atomic absorption spectrophotometer (Perkin–Elmer Zeeman/3030; Perkin–Elmer, Foster City, CA). The IR spectra (Hitachi 270-30 spectrophotometer) of the catalysts were obtained as nujol mull. TGA (DuPont 1090B thermal analyzer; DuPont, Wilmington, DE) on the catalyst or the polymer was done under nitrogen atmosphere with a heating rate of 20°C/min. The particle morphologies of the polypropylene samples were observed by SEM (JEOL JSM-820; JEOL, Peabody, MA). The specimens were deposited on SEM stubs and coated with a film of gold about 20 Å thick by sputtering techniques, to avoid electric discharges during observations.

$$Mg(OEt)_2 + nCO_2 \longrightarrow Mg(OEt)_{2-n}(\overset{\overset{\displaystyle O}{\|}}{O}COEt)_n \quad (n = 1,2)$$
$$\mathbf{I}$$
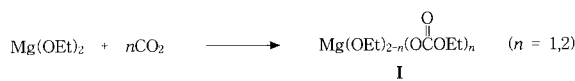
Scheme 1

RESULTS AND DISCUSSION

Structural Changes of $Mg(OEt)_2$ by Solvent Activation

The solvent activation of magnesium alkoxide in an alcohol with carbon dioxide was previously described by Arzoumanidis and Lee.[13] For example, solvent activation of the support can be performed by suspending magnesium ethoxide in ethanol, and adding carbon dioxide until the magnesium ethoxide dissolves to become a clear solution. During activation the reaction of magnesium ethoxide with carbon dioxide can be suggested, to form magnesium ethyl carbonate as illustrated in Scheme 1.

However, the structural changes of $Mg(OEt)_2$ activated by solvation of ethanol with carbon dioxide have not yet been examined in detail. To clarify the structure of magnesium ethyl carbonate (**I**), supports **1, 2,** and **3,** prepared under different conditions, were analyzed by IR and TGA and compared with the ball-milled $Mg(OEt)_2$ support.

IR spectra of ball-milled and solvent-activated magnesium supports are given in Figure 1. All of the supports equally show absorption bands at around 1400 cm^{-1}, which is assigned to the ethoxy group[6,8,9] of $Mg(OEt)_2$. Support **1,** which is obtained by removing ethanol solvent at 100°C from the clear solution of $Mg(OEt)_2$ in ethanol with CO_2, shows strong absorption bands at around 1650 and 1300 cm^{-1}, which are assigned to the carbonyl (C=O) and C—O peak of the ester[14] group, respectively. This indicates that CO_2 is directly inserted into the Mg—O bond of $Mg(OEt)_2$ by bringing it into contact with the suspension of $Mg(OEt)_2$ in ethanol, as shown in the structure of magnesium ethyl carbonate (**I**) of Scheme 1. However, supports **2** and **3,** which are prepared from the heating of support **1** at 150°C for 2 h and by the removal of ethanol solvent at 180°C from the clear solution of $Mg(OEt)_2$ in ethanol and xylene with CO_2, respectively, do not show any absorption band at around 1650 cm^{-1}, like the ball-milled $Mg(OEt)_2$ support. From these results, it is concluded that CO_2 splits off from magnesium ethyl carbonate between 100 and 150°C.
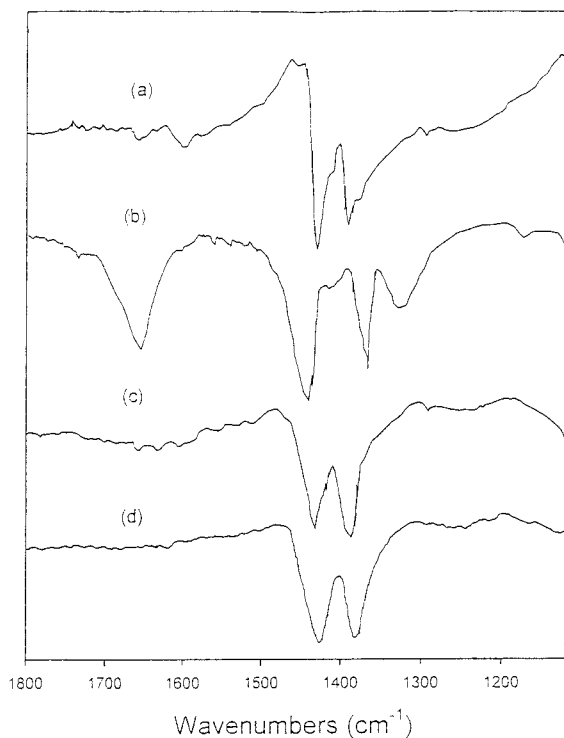
Figure 1   IR spectra of ball-milled Mg(OEt)$_2$ (a), support **1** (b), support **2** (c), and support **3** (d).

Differential TGA curves of various supports, given in Figure 2, show the dissociation temperature and amount of CO$_2$ decomposed from the magnesium ethyl carbonate. As shown in Figure 2, ball-milled Mg(OEt)$_2$ support (a) was decomposed into MgO at about 400°C with the loss of
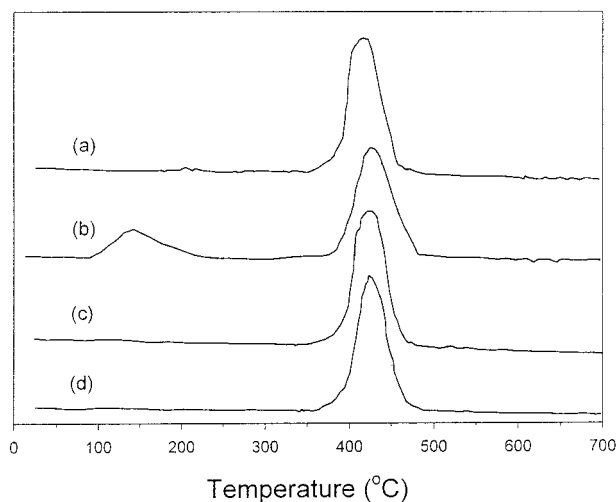

Figure 2   Differential TGA curves of ball-milled Mg(OEt)$_2$ (a), support **1** (b), support **2** (c), and support **3** (d).
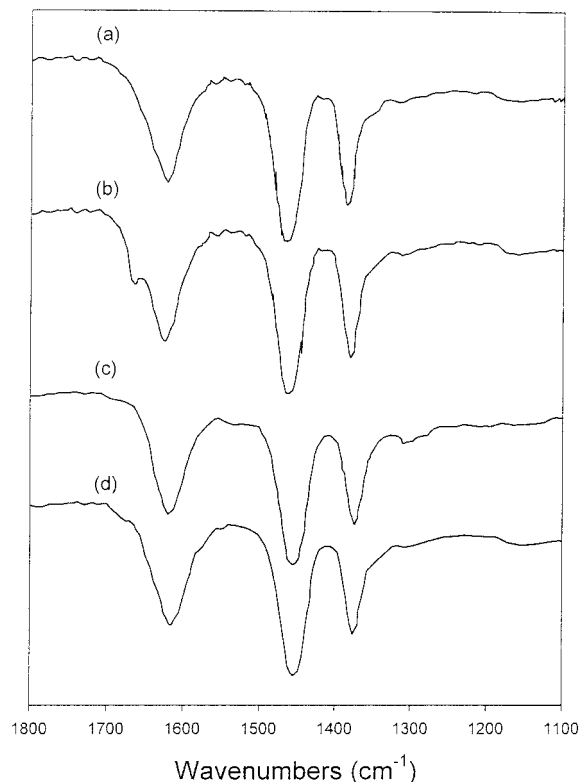

Figure 3   IR spectra of catalyst **1** (a); catalyst **3** (b); catalyst **3*** (c), obtained after retreatment of TiCl$_4$; and catalyst **4** (d).

weight. However, support **1** (b) gave the loss of weight at about 100°C as well as at 400°C. This indicates that CO$_2$ splits off at about 100°C, the amount of which was calculated from the integral TGA curves of supports; it was found that the weight loss of support **1** at about 100°C was 32–36% and the corresponding mol (n) of CO$_2$ lost was calculated to be 1.2–1.5 for structure (**I**). So, it was confirmed that 1.2–1.5 mol of CO$_2$ is associated with 1 mol of Mg(OEt)$_2$. On the contrary, supports **2** and **3** show similar TGA curves to that of the ball-milled Mg(OEt)$_2$ support. This suggested that magnesium hydrocarbyl carbonate (**I**) was converted into Mg(OEt)$_2$ when CO$_2$ was completely eliminated from support **1**.

Structures of Prepared Catalyst

IR spectra of catalysts prepared by the reaction of TiCl$_4$ with solvent-activated support as well as ball-milled Mg(OEt)$_2$ support are given in Figure 3. All catalysts [(a)–(d)] show absorption bands at 1630 cm^{-1} assigned to the peak of MgCl$_2$ because Mg(OEt)$_2$ is converted to MgCl$_2$ by reacting with TiCl$_4$.[6,8,15] However, catalyst **3** (b), which is ob-
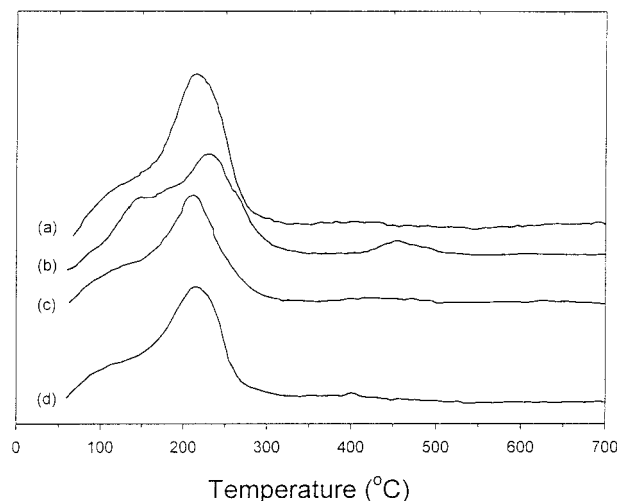
Figure 4 Differential TGA curves of catalyst **1** (a); catalyst **3** (b); catalyst **3*** (c), obtained after retreatment of $TiCl_4$; and catalyst **4** (d).

tained by the reaction of support **1** with $TiCl_4$, shows not only the characteristic peak of $MgCl_2$ at 1630 cm^{-1} but also the carbonyl (C=O) peak at 1650 cm^{-1} derived from support **1**. In the case of catalyst **3*** (c), obtained after retreatment of $TiCl_4$, the carbonyl peak at 1650 cm^{-1} disappeared and only the peak of $MgCl_2$ showed at 1630 cm^{-1}. From the preceding results, it was confirmed that CO_2 partially split off from magnesium hydrocarbyl carbonate when support **1** was first treated with $TiCl_4$ and then was completely eliminated by retreatment of $TiCl_4$. Catalyst **4** (d) showed a similar IR spectrum to that of catalysts **1** (a) and **3*** (c), with the $MgCl_2$ peak at 1630 cm^{-1}.

TGA chromatograms of catalysts **1, 3, 3*,** and **4** were obtained to investigate the structure of the catalysts in detail, as shown in Figure 4. Catalyst **1** (a), catalyst **3*** (c), and catalyst **4** (d) show the weight losses only at 200°C, attributed to the decomposition[6] of $MgCl_2$ obtained by the reaction of $Mg(OEt)_2$ with $TiCl_4$. On the contrary, catalyst **3** (b) shows weight losses at around 140, 225, and 450°C, respectively. This result seems to be caused by the presence of CO_2 in catalyst **3**. The weight losses at around 140 and 450°C are derived from the loss of CO_2 remaining even at 200°C and decomposition of $Mg(OEt)_2$, respectively, whereas the weight loss at around 225°C is derived from the decomposition of $MgCl_2$.
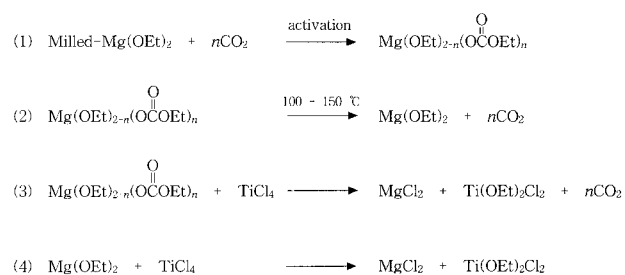
From these findings it seems possible to draw general conclusions on the structural changes of the $Mg(OEt)_2$ support by solvent activation. We can rationalize the interactions among the cata-

lytic system components with the following reaction model (Scheme 2).

Equation (1) of Scheme 2 is a procedure for solvent activation. A 1.2–1.5 mol (n) sample of CO_2 can be associated with 1 mol of $Mg(OEt)_2$. CO_2 is decomposed from the obtained magnesium ethyl carbonate between 100 and 150°C and modified $Mg(OEt)_2$ is produced . Both solvent-activated magnesium ethyl carbonate and $Mg(OEt)_2$ are converted to $MgCl_2$ by reacting with $TiCl_4$ [eqs. (3) and (4)].[6,8,15]

Investigations on the role of Lewis base as electron donor used in the preparation of a highly active and highly stereospecific $MgCl_2$/$TiCl_4$ catalyst for propylene polymerization were previously reported in some detail by many authors.[16–19] It was found that suitable amounts of Lewis base increased the yield of isotactic polymers, but at the same time decreased very sharply the yield of atactic polymers, and consequently the stereospecificity of the resulting polymer was enhanced. In addition, Gerbasi et al.[20] reported that ethyl benzoate (EB) as internal donor (ID) transformed $MgCl_2$ particles into small sizes, which gave high concentration of active sites and high stereospecificity if crystal faces of $MgCl_2$ were treated with EB. Moreover, in a previous study[8] we reported that benzoyl chloride (BC) as ID was converted to EB when BC was brought into contact with $Mg(OEt)_2$/$TiCl_4$ catalyst.

IR spectra of $Mg(OEt)_2$/$TiCl_4$ (catalyst **4**), $Mg(OEt)_2$/EB/$TiCl_4$ (catalyst **6**), and $Mg(OEt)_2$/BC/$TiCl_4$ (catalyst **7**) are given in Figure 5. The IR spectra of catalysts **6** and **7** are similar, in which the characteristic peak of $MgCl_2$ appears at[6,8] about 1630 cm^{-1} and the C=O peak of EB shifts from about 1720 to 1680 cm^{-1} as a result of coordination with the catalyst.[21,22] On the other hand, the CO—Cl peak of BC is barely observed at about 1780 cm^{-1} in the $Mg(OEt)_2$/BC/$TiCl_4$ system (catalyst **7**) as a result of the exchange reaction of the chlorine of BC with the ethoxy group of $Mg(OEt)_2$ during the reaction of $TiCl_4$.[8]
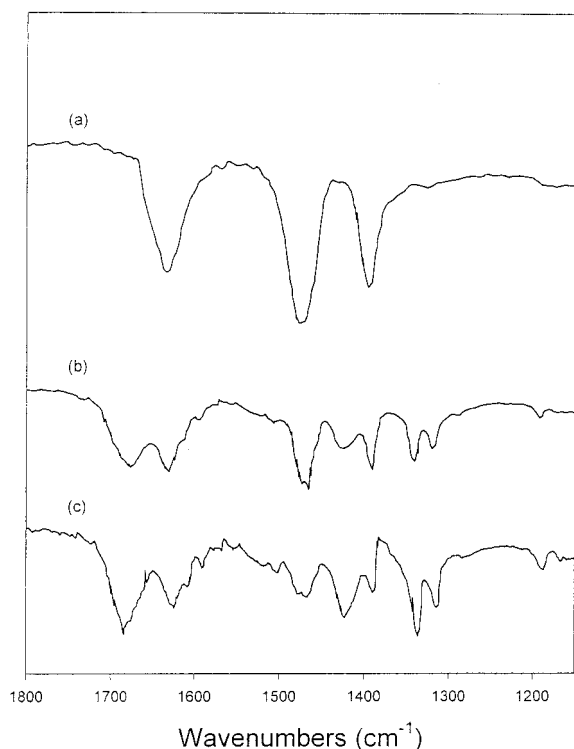
(1)   Milled–$Mg(OEt)_2$ + nCO_2 $\xrightarrow{activation}$ $Mg(OEt)_{2-n}(O\overset{O}{\overset{\|}{C}}OEt)_n$

(2) $Mg(OEt)_{2-n}(O\overset{O}{\overset{\|}{C}}OEt)_n$ $\xrightarrow{100 \sim 150 \,℃}$ $Mg(OEt)_2$ + nCO_2

(3) $Mg(OEt)_{2-n}(O\overset{O}{\overset{\|}{C}}OEt)_n$ + $TiCl_4$ $\dashrightarrow$ $MgCl_2$ + $Ti(OEt)_2Cl_2$ + nCO_2

(4) $Mg(OEt)_2$ + $TiCl_4$ $\longrightarrow$ $MgCl_2$ + $Ti(OEt)_2Cl_2$

Scheme 2

Figure 5 IR spectra of catalyst **4** (a), catalyst **6** (b), and catalyst **7** (c).

Table I   Results of Propylene Polymerization by Solvent-Activated Mg(OEt)$_2$/TiCl$_4$ Catalysts Without ED

Catalyst	Ti (wt %)	Activity[a]	Isotactic Index (wt %)
1	12.7	2.0	48.5
2	20.0	Trace	—
3	10.4	1.3	49.1
3* [b]	8.4	1.7	50.9
4	12.4	1.6	50.0
4* [b]	10.0	2.4	51.0
5	12.0	1.6	50.1

Polymerization conditions: molar ratio of [Al]/[Ti] = 150, 1 atm, 50°C, 2 h.

[a] K_g of PP/g of Ti atm^{-1} h^{-1}.

[b] **3***,**4***: Retreatment of **3** and **4** with TiCl$_4$, respectively.

From the TGA curves of catalysts **4, 6,** and **7,** as shown in Figure 6, both catalyst **6** (b) and catalyst **7** (c) display two distinct peaks at around 230 and 520°C in addition to weak peaks at around 150 and 450°C, whereas catalyst **4** (a) exhibits a peak appearing at 200°C as a result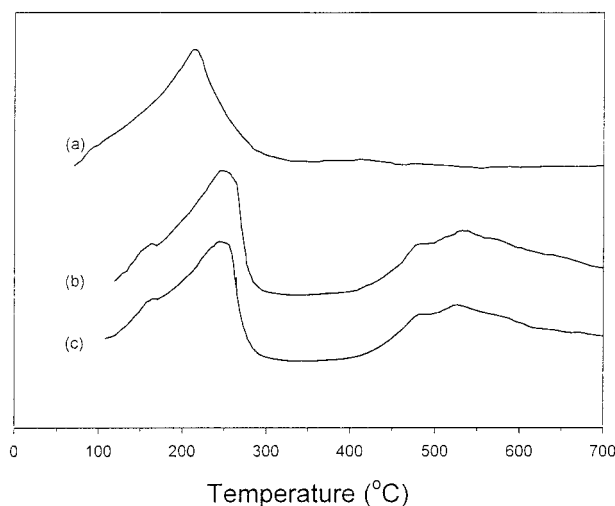 of the decomposition of MgCl$_2$; these peaks are con-sidered to be attributable to EB.[21] The weak peaks at around 150 and 450°C are attributed to ED having little or no interaction with MgCl$_2$; therefore, the peaks at around 230 and 520°C are caused by EB having, respectively, weak and strong interactions with MgCl$_2$.[21]

In conclusion, the prepared Mg(OEt)$_2$/ID/TiCl$_4$ catalyst systems, which use the Mg(OEt)$_2$ support activated by solvation of ethanol with CO$_2$, show similar characteristics in their structure to those of the ball-milled Mg(OEt)$_2$/ID/TiCl$_4$ catalyst systems reported in previous studies.[6–8,21,22]

Polymerization Behaviors for Propylene

Propylene polymerizations with ball-milled Mg(OEt)$_2$-supported TiCl$_4$ catalysts were exam-ined in detail in previous studies.[6–12] Results of propylene polymerization by the present catalyst prepared by using solvent-activated Mg(OEt)$_2$ support under various conditions are given in Ta-ble I. Catalyst **2** shows high Ti content but does not exhibit activity as a result of the formation[7,23] of inactive alkoxy compounds of titanium from the reaction of TiCl$_4$ and EtOH. Catalyst **3,** pre-pared using support **1,** is low in both Ti content and activity compared to that in catalysts **1, 4,** and **5,** which are prepared by using ball-milled Mg(OEt)$_2$, supports **2** and **3,** respectively. This indicates that the low Ti content of catalyst **3** results from the presence of the carbonyl group in the catalyst by insertion of CO$_2$ and the resulting catalyst also gives slightly low activity.

However, if catalysts **3** and **4** are retreated with TiCl$_4$, the corresponding catalysts (see cata-lysts **3*** and **4***) exhibit not only a decrease of Ti

Figure 6 Differential TGA curves of catalyst **4** (a), catalyst **6** (b), and catalyst **7** (c).

Table II   Results of Propylene Polymerization by Solvent-Activated Mg(OEt)$_2$/ID/TiCl$_4$ Catalysts

Catalyst	Retreatment of TiCl$_4$	Ti (wt %)	Without ED		With PTES as ED	
			Activity[a]	Isotactic Index (wt %)	Activity[a]	Isotactic Index (wt %)
6	None	5.0	15.1	58.1	3.7	82.4
[Mg(OEt)$_2$/EB/TiCl$_4$]	Once	3.9	17.5	59.1	4.1	83.0
7	None	4.2	14.7	58.9	3.2	83.0
[Mg(OEt)$_2$/BC/TiCl$_4$]	Once	3.5	17.1	60.0	3.4	83.2

Polymerization conditions: molar ratio of [Al]/[Ti] = 150, [ED]/[Al] = 0.05, 1 atm, 50°C, 2 h.
[a] Activity = K_g of PP/g of Ti atm^{-1} h^{-1}.

content but also an increase of activity, as shown in Table I. This seems to be attributed to the removal of alkoxy compounds of titanium, which have less activity for propylene polymerization.[7,23]

The effects of ID and external donor (ED) on catalyst activity and isotacticity of polymer obtained for propylene polymerization with solvent-activated Mg(OEt)$_2$/ID/TiCl$_4$ catalysts are given in Table II. Compared with the solvent-activated Mg(OEt)$_2$/TiCl$_4$ catalysts (**4** and **5** in Table I), the solvent-activated Mg(OEt)$_2$/ID/TiCl$_4$ catalysts (**6** and **7** in Table II) show remarkable increases in activity with decreasing Ti content as a result of the increase of surface area in particles by complexing of MgCl$_2$ and ID.[7,24] However, the solvent-activated Mg(OEt)$_2$/ID/TiCl$_4$ catalysts also show tendencies in retreatment of TiCl$_4$ with decreasing Ti content and increasing activity similar to those of the solvent-activated Mg(OEt)$_2$/TiCl$_4$ catalysts shown in Table I. On the other hand, the use of an ED increases the relative amount of isotactic polymer, while decreasing the catalyst activity. This was explained in previous studies[6,25,26]: the sterically hindered external silane donor was selectively coordinated to one of the vacancies of atactic sites, followed by deactivation of the catalyst and formation of the highly isospecific species, which produced high isotactic polymers.

From these results, it is concluded that the solvent-activated Mg(OEt)$_2$-supported catalyst systems, using supports that are newly prepared by the solvent-activated Mg(OEt)$_2$ with ethanol and CO$_2$, show polymerization behaviors that are similar to those of the ball-milled Mg(OEt)$_2$-supported catalyst systems.
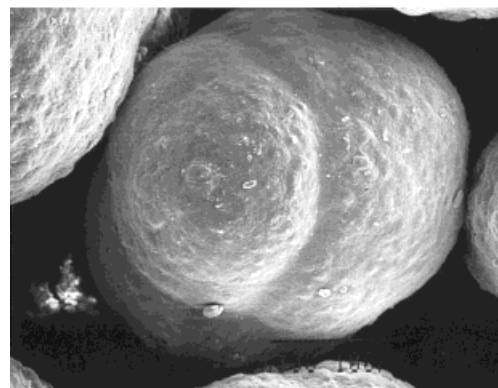
Morphology

In Ziegler–Natta catalysts, it was previously established that the polymer granules produced in propylene polymerization replicate the shape of the catalyst particles.[27–29] There are distinct commercial advantages in using spherical catalyst particles of narrow particle size distribution and, as a result, there has been considerable effort in recent years to prepare catalysts in spherical form.

SEM micrographs were obtained to observe polymer morphology, as shown in Figure 7. The
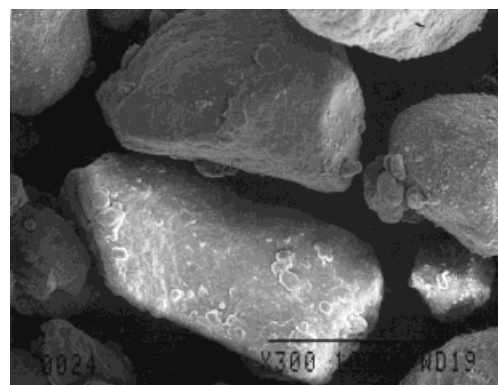
(a)

(b)

Figure 7 SEM micrographs of polypropylene obtained with (a) ball-milled Mg(OEt)$_2$ and (b) solvent-activated Mg(OEt)$_2$ support, ×300 magnification.

morphology of polymer obtained by ball-milled Mg(OEt)$_2$-supported catalyst (a) was irregular, whereas solvent-activated Mg(OEt)$_2$-supported catalyst (b) gives spherical-type polymer morphology, thus potentially confirming that the original structure of ball-milled Mg(OEt)$_2$ is changed from the irregular form to the spherical form by the reaction of Mg(OEt)$_2$ with ethanol and CO$_2$, after which globular support is obtained.

CONCLUSIONS

The structural changes of Mg(OEt)$_2$ support by solvent activation with ethanol and carbon dioxide are as follows: (1) 1.2–1.5 mol (n) of CO$_2$ can be associated with 1 mol of Mg(OEt)$_2$. (2) CO$_2$ is decomposed from the obtained magnesium ethyl carbonate between 100 and 150°C, and modified Mg(OEt)$_2$ is produced. (3) Both solvent-activated magnesium ethyl carbonate and Mg(OEt)$_2$ are converted to MgCl$_2$ by reacting with TiCl$_4$. The prepared Mg(OEt)$_2$/ID/TiCl$_4$ catalyst systems, using the Mg(OEt)$_2$ support activated by solvation of ethanol with CO$_2$, show similar characteristics in their structure and polymerization behavior to those of the ball-milled Mg(OEt)$_2$/ID/TiCl$_4$ catalyst systems. However, the solvent-activated Mg(OEt)$_2$-supported catalyst systems show spherical-type polymer morphology compared to that of the ball-milled Mg(OEt)$_2$-supported catalyst systems.

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