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Preparation of Inorganic $MgCl_2$-Alcohol Adduct and Its Application in Organometallic HYBRID Catalysts for Ethylene Polymerization

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Abstract–Inorganic support, $MgCl_2$-alcohol adduct, for use in the impregnation of organometallic catalysts, was prepared by the recrystallization method using alcohol. Since $MgCl_2$-alcohol adduct has two functional groups in the molecule, i.e., hydroxyl (-OH) and chlorine (-Cl) groups, it is suitable for the impregnation of both metallocene and Ziegler-Natta hybrid catalysts. The hybrid catalysts were prepared in order to control the molecular weight (Mw) and the molecular weight distribution (MWD) in ethylene polymerization. The polyethylene produced by the Ziegler-Natta/Metallocene hybrid catalysts showed two melting temperatures and a bimodal MWD, corresponding to products arising from each of the individual catalysts. This suggests that these hybrid catalysts acted as individual active species and produced a blend of polymers.

Key words: $MgCl_2$-Alcohol Adduct, Recrystallization, Metallocene, Ziegler-Natta, Ziegler-Natta/Metallocene Hybrid Catalysts, Ethylene Polymerization

INTRODUCTION

In early 1980, metallocene catalyst attracted much attention as the next generation of catalysts for olefin polymerization [Sinn and Kaminsky, 1980]. Such systems show a high activity and are capable of producing polymers with special properties that are unattainable via Ziegler-Natta catalyst [Kaminsky et al., 1991; Ishihara et al., 1988; Zambelli et al., 1991]. The metallocene catalysts are basically homogeneous, and the majority of studies on such catalysts have concentrated on solution phase processes. However, for the metallocene catalysts to be used in the prevailing slurry or gas phase processes, a procedure for the impregnation of a metallocene is necessary. In recent papers, a variety of supports such as SiO_2, Al_2O_3, and Zeolite, have been used [Soga and Kaminaka, 1992, 1994; Woo et al., 1986; Cho et al., 2000; Kim et al., 1990]. Although metallocene catalysts have the advantages of high activity and special polymer properties, the polymers produced via these catalysts have a very narrow molecular weight distribution (MWD, Mw/Mn).

In polymer processing, the molecular weight (Mw) and the molecular weight distribution (MWD) represent basic properties, which serve as major determinants of polymer properties. Mw largely relates to determinant of mechanical properties, while MWD is largely responsible for rheological properties. High Mw polymer has improved physical properties, but also is difficult to process. On the other hand, an increase in MWD tends to improve flowability at high shear rate, which is important for blowing and extrusion techniques [Cho et al., 1998, 2001; Razavi, 1999; Ko et al., 1999]. Therefore, it is necessary to control the Mw, as well as the MWD of polymers in order to optimize both the mechanical and the rheological properties.

Several methods for controlling the Mw and the MWD of polymers are available. The first method involves physically blending the polymers of different average Mw. However, polymer blends have high gel levels, and, as a result, miscibility problems can occur. The second method involves the use of a series of reactors, each of which involves different polymerization conditions, such as temperature and pressure. This method is unacceptable because it involves additional processes, thus increasing capital costs. The third method is to combine two or more catalysts in a single reactor, thereby producing polymers with different Mw ranges. In this case, a highly advanced catalyst technology is required. Most studies in this area have dealt with the use of homogeneous catalyst mixtures [Ahlers and Kaminsky, 1988; Dagnillo et al., 1998]. However, a limited number of reports have been published which deal with MWD in heterogeneous catalysts [Cho et al., 2000]. From the practical viewpoint of polymer processes, in order for the catalysts to be used in the commercial slurry or gas phase processes, it is necessary to modify them to a heterogeneous form.

In this study, which is based on the above rationale, heterogeneous Ziegler-Natta/Metallocene hybrid catalysts were prepared in order to control the MWD of polyethylene. It is conceivable that polymer blends of a low Mw produced by a metallocene and a high Mw by a Ziegler-Natta affect Mw and MWD. For the impregnation of these two types of organometallic catalysts, $MgCl_2$ was modified via the recrystallization method by using alcohol. $MgCl_2$-alcohol adduct has two functional groups in the molecule, i.e., hydroxyl (-OH) in alcohol and chlorine (-Cl) groups in magnesium dichloride, it could be suitable for the impregnation of both metallocene and Ziegler-Natta catalysts. The prepared support and the hybrid catalysts were characterized by ICP, TGA, GC, etc. and the ethylene polymerization was conducted in order to investigate the char-

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‡This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

acteristics of the hybrid catalysts.

EXPERIMENTAL

1. Materials

High purity N_2 and ethylene (Sinyang Gas Products) were further purified prior to use by sequentially passing them through columns containing 5 Å molecular sieves (Kokusan Chem.), anhydrous P_2O_5 (Yakuri Chem.), and RIDOX, an oxygen scavenger (Fischer scientific). Toluene (Oriental Chemical Industry) used as a solvent for the catalyst preparation and polymerization was purified by distillation over elemental sodium under an N_2 atmosphere to remove residual traces of moisture. $MgCl_2$ (Aldrich Chem.), CH_3OH (Carlo Erba.), n-decane (Junsei Chem.), Cp_2ZrCl_2 (Strem Chem.), $TiCl_4$ (Aldrich Chem.), TIBAL (triisobutylaluminum; Aldrich Chem.), TEA (triethylaluminium; Aldrich Chem.), TMA (trimethylaluminum; Aldrich Chem.), MAO (methylaluminoxane; type 4, Akzo Chem.) were used without further purification.

2. Preparation of Support and Catalyst

0.10 mole (9.52 g) of anhydrous $MgCl_2$ was introduced into a glass reactor equipped with a magnetic stirrer and 100 mL of methanol was added. The mixture was heated to 60 °C and stirred until the $MgCl_2$ had completely dissolved. 100 mL of n-decane was then added to this homogeneous solution and the final mixture was stirred at 2,000 rpm. under vacuum at 80 °C. $MgCl_2$ particles were slowly precipitated in the n-decane medium as the methanol evaporated. The resulting $MgCl_2$ particles were washed several times with toluene to remove residual n-decane and then dried under vacuum to remove the toluene. Thus, the recrystallized $MgCl_2$ ($MgCl_2 \cdot nCH_3OH$) was obtained [Park and Lee, 1992]. 5 g of these supports were introduced into a 500 mL flask equipped with a magnetic stirrer. 100 mL of toluene was added and then, the alkylaluminum compound was added to the flask. The mixture was stirred at 0, 20, 40, 60 °C for 30 minutes, respectively and then stirred at 80 °C for two hours. The mixture was then washed to remove the unreacted alkylaluminum and finally dried under vacuum to give the alkylaluminum/$MgCl_2 \cdot nCH_3OH$. 2 g of the washed supports were suspended in 100 mL of toluene and reacted with 0.10 g of Cp_2ZrCl_2 at 50 °C for 2 hours and then washed in the same manner (Cp_2ZrCl_2/alkylaluminum/$MgCl_2 \cdot nCH_3OH$. 5 mL of $TiCl_4$ was introduced into supported metallocene catalyst, and the mixture was stirred for two hours at 80 °C. After the reaction, the mixture was washed several times with toluene to give the final Ziegler-Natta/Metallocene hybrid catalysts. These hybrid catalysts, denoted as $TiCl_4$/Cp_2ZrCl_2/alkylaluminum compound/$MgCl_2 \cdot nCH_3OH$, were suspended in 100 mL of toluene and used as catalysts.

3. Characterization

To determine the alcohol contents in the recrystallized $MgCl_2$, gas chromatography (GC; Yanaco G1700, Porapak Q column) and thermogravimetric analysis (TGA; Perkin-Elmer, TGA7) were used. For GC method, the alcohol contents were determined by comparing the detected peak of the recrystallized $MgCl_2$ in alcohol solution with that of alcohol. In TGA analysis, based on the weight reduction in the support via thermal treatment under N_2, the alcohol contents were calculated. The titanium and zirconium contents of the catalysts were measured by using inductively coupled plasma (ICP; VG PQ2-Turbo, VG elemental). The differential scanning calorimetry (DSC; Dupont V4.0B) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min. The molecular weight and molecular weight distribution of polyethylene were measured by gel permeation chromatography (GPC; PL-210, Polymer Laboratory Ltd.) at 160 °C with 1,2,4-trichlorobenzene as the solvent.

4. Ethylene Polymerization

300 mL of toluene and cocatalyst (MAO or alkylaluminum compound) were introduced into a 1 L glass reactor, equipped with a magnetic stirrer under a stream of N_2 and then evacuated to remove the N_2. Ethylene was then fed at a constant pressure of 1.3 bar containing a hydrogen partial pressure of 0.2 bar. The polymerization was initiated by introducing the catalyst suspension into the reactor with a syringe. After a 50 min reaction time, the polymerization was terminated by the addition of the dilute hydrochloric acid solution and the polymer was isolated and dried. The polymerization rate was determined from the amount of consumed ethylene, measured by using a mass flowmeter.

RESULTS AND DISCUSSION

1. Characteristics of $MgCl_2$ Prepared by the Recrystallization Method

Anhydrous $MgCl_2$ has a cubic close packing (ccp) structure which gives a strong XRD pattern at 2θ=15° (003), 35° (004) and 50° (110 plane) [Magalhaes et al., 1991]. However, the XRD patterns vary depending on the condition of the support. It was found that the peak intensities of the recrystallized $MgCl_2$ were weaker compared with those of anhydrous $MgCl_2$ as shown in Fig. 1(b), suggesting that $MgCl_2 \cdot nCH_3OH$ was formed during the preparation of the $MgCl_2$ by the recrystallization method. Based on the calculated methanol

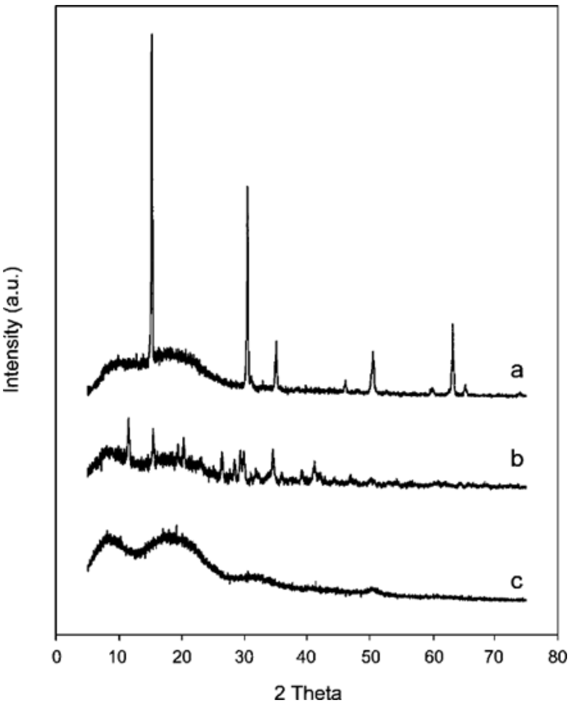

Fig. 1. XRD patterns of the recystallized $MgCl_2$.
(a) anhydrous $MgCl_2$, (b) $MgCl_2 \cdot 4CH_3OH$, (c) TIBAL/$MgCl_2 \cdot 4CH_3OH$

Table 1. Methanol and methoxy contents in the supports

Support	GC (wt%)	TGA (wt%)	
	Methanol+Methoxy (CH_3OH) (Mg-OCH_3)	Methanol[a] (CH_3OH)	Methoxy[b] (Mg-OCH_3)
$MgCl_2 \cdot 4CH_3OH$	57.9	38.6	16.4
$MgCl_2 \cdot 4CH_3OH$-100 °C	30.4	9.2	18.1
$MgCl_2 \cdot 4CH_3OH$-200 °C	23.8	4.5	17.5

[a] Weight reduction from 30 °C to 200 °C.
[b] Weight reduction from 200 °C to 300 °C.

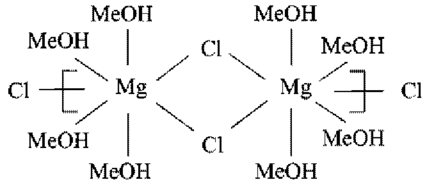

Fig. 2. The proposed structure of the recrystallized $MgCl_2 \cdot 4CH_3OH$.

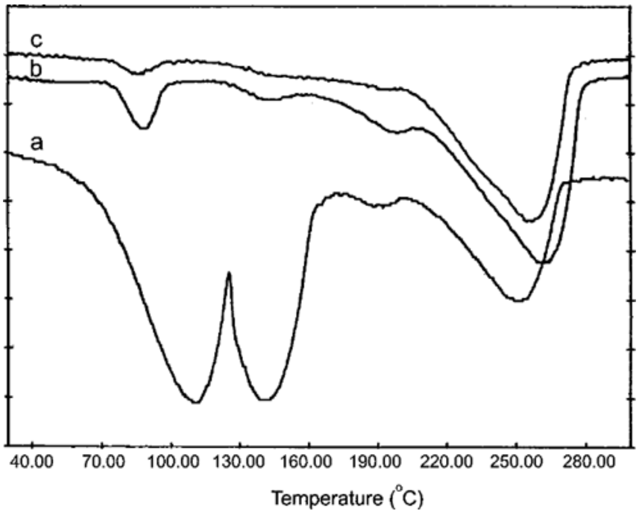

Fig. 3. DTGA thermograms of supports.
(a) recrystallized $MgCl_2 \cdot 4CH_3OH$, (b) $MgCl_2 \cdot 4CH_3OH$-100 °C, (c) $MgCl_2 \cdot 4CH_3OH$-200 °C

content in Table 1, the approximate value of n is 4 by converting the weight percentage of the methanol into the moles. Fig. 2 shows the proposed structure of the $MgCl_2 \cdot 4CH_3OH$.

To examine the desorption temperature of methanol, the support was scanned from 30 °C to 300 °C by TGA under an N_2 atmosphere, and DTGA thermograms were obtained by differentiating TGA thermograms. Fig. 3 shows the DTGA thermograms of the supports, which were prepared at various temperatures. The methanol in the non-thermal treated $MgCl_2 \cdot 4CH_3OH$ desorbed at around 110, 140, and 250 °C, respectively, thus giving the methoxy groups in the support as shown in Eq. (1) [Magalhaes et al., 1991].

The methanol contents in the thermal treated supports decreased drastically with increasing treatment temperature. However, the levels of methoxy groups at about 250 °C produced by the methanol desorption as shown in Eq. (1) remained constant. This suggests that considerable amounts of methoxy groups exist in the support after thermal pretreatment. Table 1 shows the methanol and methoxy contents as analyzed by GC and TGA. The contents of methanol plus methoxy are nearly the same for both GC and TGA analyses.

$$MgCl_2 \cdot 4CH_3OH \rightarrow MgCl_X(OCH_3)_Y + mHCl + nCH_3OH \; (m+n=4,\ X+Y=2) \qquad (1)$$

2. Effect of Support Pretreatment on the Impregnation of the Metallocene Catalyst

It is well known that if metallocene catalyst is directly impregnated on supports without any modification of their surfaces, the catalytic activity and the degree of impregnation are typically low [Soga and Kaminaka, 1992]. MAO or other alkylaluminum compounds such as TIBAL and TMA acting as an anchor between the metallocene catalyst and the support were used to modify the inorganic support for the impregnation of the metallocene catalyst [Soga and Kaminaka, 1991]. In this study, the surface condition of the recrystallized $MgCl_2$ was modified by treatment with various common alkylaluminums such as TMA, TEA, TIBAL and MAO. As shown in Table 2, it was necessary for the support to be pretreated with an alkylaluminum compound in order to create an appropriate impregnation site. When an alkylaluminum compound is used as a pretreatment reagent, TIBAL is effective for impregnating Cp_2ZrCl_2 catalyst to create potential, catalytic sites.

Fig. 1(c) shows that, when the recrystallized $MgCl_2$ was treated with TIBAL, the XRD peaks disappeared as a result of the removal of methanol in the form of aluminum methoxide, which arose via the reaction of TIBAL with methanol in the support.

The results in Table 2 show that the impregnated content of Cp_2ZrCl_2 increased with increasing levels of TIBAL pretreatment, and that the surface area drastically increased as well. To evaluate the influence of methanol in the support on the impregnation of Cp_2ZrCl_2, the supports were thermally pretreated at 100 and 200 °C, respectively, followed by the reaction with TIBAL. In this case, however, a small amount of Cp_2ZrCl_2 was impregnated. This is because some of the methanol in the support was converted to methoxy groups, which do not serve as the impregnation sites, as shown in Eq. (1).

It is noteworthy that the modification of the recrystallized $MgCl_2$ by pretreatment with TIBAL provides for the impregnation sites of the metallocene catalyst. Thus, it is concluded that these chemical complexes produced by the reaction between methanol and alkylaluminum create the impregnation sites for Cp_2ZrCl_2. The plausible impregnation mechanism of the metallocene catalysts is shown in Fig. 4.

3. Effect of Methanol and Methoxy Groups on Supporting Ziegler-Natta/Metallocene Hybrid Catalysts

Table 2. Characteristics of $MgCl_2$ prepared by the recrystallization method and various catalysts

Supports and catalysts	Alcohol content (wt%)	Surface area (m^2/g)	Pretreatment concentration (mole/L)	Zr (wt%)	Ti (wt%)
anhydrous $MgCl_2$	-	1.7	-	-	-
$MgCl_2\cdot 4CH_3OH$	56.5	14.1	-	-	-
$MgCl_2\cdot 4CH_3OH$-100 °C	13.4	16.8	-	-	-
$MgCl_2\cdot 4CH_3OH$-200 °C	7.21	20.5	-	-	-
$Cp_2ZrCl_2/TMA/MgCl_2\cdot 4CH_3OH$	-	n.d	0.6	0.056	-
$Cp_2ZrCl_2/TEA/MgCl_2\cdot 4CH_3OH$	-	n.d	0.6	0.44	-
$Cp_2ZrCl_2/MAO/MgCl_2\cdot 4CH_3OH$	-	n.d	0.6	0.14	-
$Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$-100 °C	-	42.3	0.3	0.012	-
$Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$-200 °C	-	39.8	0.2	-	-
$Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$	-	382.1	0.6	1.02	-
		209.4	0.3	0.43	-
		68.3	0.15	-	-
$TiCl_4/Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$	-	428.5	0.6	0.87	2.47
$TiCl_4/TIBAL/MgCl_2\cdot 4CH_3OH$	-	412.7	0.6	-	2.88

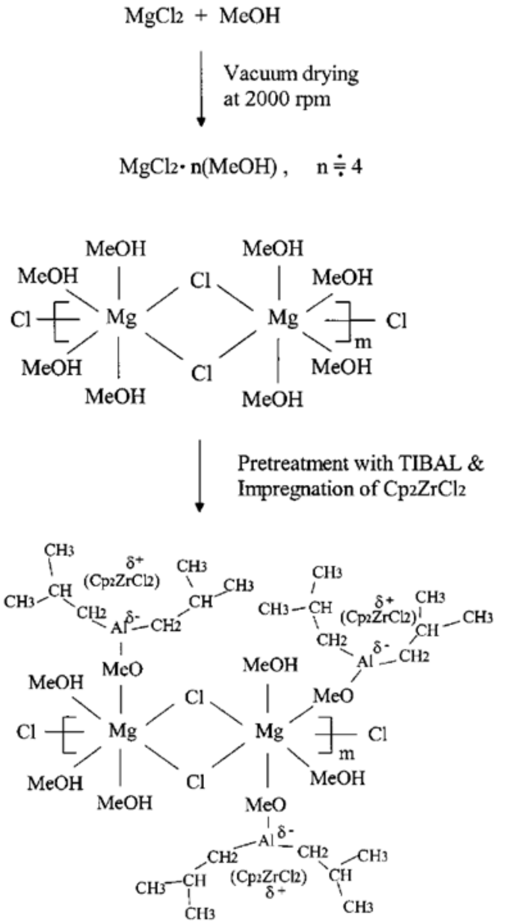

Fig. 4. Proposed mechanism for the impregnation of the metallocene catalysts over the recystallized $MgCl_2$.

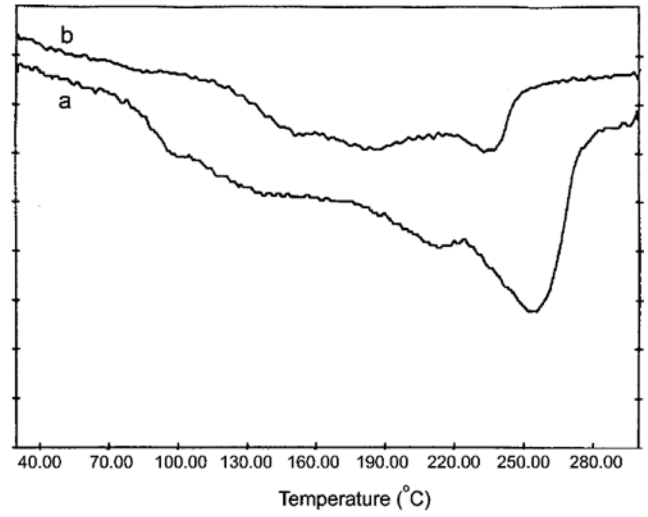

Fig. 5. DTGA thermograms of catalysts.
(a) $Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$, (b) $TiCl_4/Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$

After the support was impregnated with Cp_2ZrCl_2, the Ziegler-Natta/Metallocene hybrid catalysts were prepared by reacting the metallocene supported catalyst with $TiCl_4$. To evaluate the influence of methanol and methoxy groups on catalyst impregnation, TGA was performed. Fig. 5 shows that the methoxy contents in the impregnated Cp_2ZrCl_2 catalyst remained constant, but decreased during the reaction with $TiCl_4$. Methoxy groups, which exist in the recrystallized $MgCl_2$ and were also produced by reaction between methanol in the support and TIBAL, create the impregnation sites for $TiCl_4$. This indicates that the methanol content in the support partly affects the impregnation of Cp_2ZrCl_2, and the methoxy groups partly affect that of $TiCl_4$ in the hybrid catalysts.

4. Polymerization of Ethylene

Table 3 shows the results of ethylene polymerization over the homogeneous metallocene catalyst (Cp_2ZrCl_2), the supported metallocene catalyst ($Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$), the supported hybrid catalysts ($TiCl_4/Cp_2ZrCl_2/TIBAL/MgCl_2\cdot 4CH_3OH$) and the supported Ziegler-Natta catalyst ($TiCl_4/TIBAL/MgCl_2\cdot 4CH_3OH$). In comparing the activities of the homogeneous metallocene catalyst to those of the metallocene supported catalyst with MAO co-

Table 3. Analytical data on the polyethylene produced by various $MgCl_2$ supported catalysts

Catalysts	Cocatalyst	Mole ratio (Al/[Metal])	Activity*	Tm (°C)	Xc (%)**	Mw ($\times10^{-5}$)	MWD
Cp_2ZrCl_2	MAO	Al/Zr=1000	4655.0	125.8	79.6	0.13	2.1
	MAO	Al/Zr=3000	34532.2	124.9	78.9	0.15	2.1
Cp_2ZrCl_2/TIBAL/$MgCl_2\cdot4CH_3OH$	MAO	Al/Zr=3000	2535.7	127.8	73.8	0.46	3.4
$TiCl_4$/Cp_2ZrCl_2/TIBAL/$MgCl_2\cdot4CH_3OH$	MAO	Al/Zr=3000	15720.6	126.4/135.3	68.9	6.81	9.7
	MAO TEA	Al/Zr=3000 Al/Ti=50	16833.5	134.8	64.8	7.04	6.8
	TEA	Al/Ti=300	893.8	135.1	65.4	7.69	5.9
$TiCl_4$/TIBAL/$MgCl_2\cdot4CH_3OH$	TEA	Al/Ti=300	923.4	134.9	62.0	7.80	6.0
	MAO	Al/Ti=2000	7996.3	137.8	64.5	8.25	6.5

Conditions: Tp=70 °C; P_{C2H4}=1.3 atm; P_{H2}=0.2 atm.
*Activity: kg-HDPE/mole-[Metal]·atm·hr.
**Crystallinity: Xc (%)=100 (ΔHm/ΔHm*); ΔHm*=282.84 J/g.

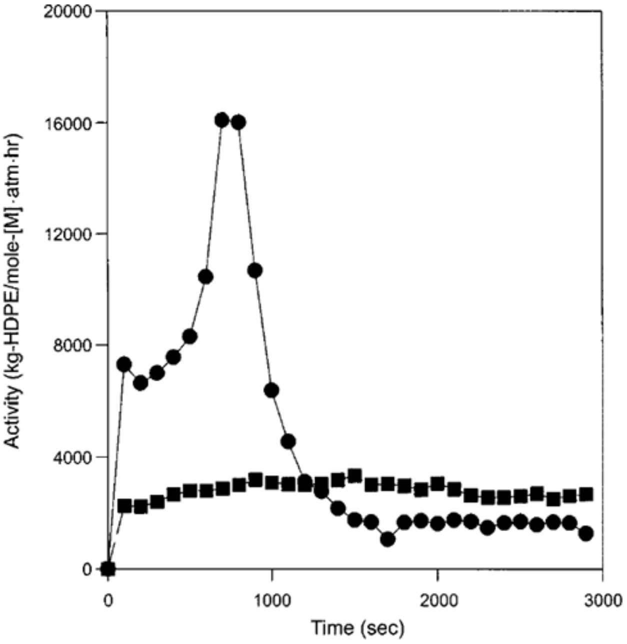

Fig. 6. Plot of rate versus time for the polymerization of ethylene over Cp_2ZrCl_2 catalyst systems: (●) Cp_2ZrCl_2, MAO (Al/[M]=1000); (■) Cp_2ZrCl_2/TIBAL/$MgCl_2\cdot4CH_3OH$, MAO (Al/[M]=3000). **Polymerization conditions: Tp=70 °C; P_{C2H4}=1.3 atm; P_{H2}=0.2 atm.

catalyst, the activity decreases due to the relatively low activity characteristics of the metallocene supported catalyst. When the activity profiles of the homogeneous and the heterogeneous metallocene catalysts are compared, there is a great deal of difference between the two catalysts. Fig. 6 shows that the activity of the homogeneous metallocene catalyst drastically decreases after 15 minutes, but that of the metallocene supported catalyst remains constant for up to one hour. The main reason for this behavior is probably due to the stability increase of the supported catalyst during the polymerization.

In DSC analyses, the crystallinity (Xc) decreases from the homogeneous metallocene to the Ziegler-Natta supported catalyst because Ziegler-Natta catalyst produces irregular polyethylene chains. The melting temperature of the polymer produced by the metallocene supported catalyst was approximately 130 °C, while, for the Ziegler-Natta supported catalyst, it was approximately 140 °C. The difference in melting temperature between the polymers produced by Cp_2ZrCl_2 and by $TiCl_4$ is due to the fact that melting temperature increases in proportion to the higher molecular weight and lamellar thickness.

Since the hybrid catalysts have two different active sites, the polymers produced via the hybrid catalysts with MAO cocatalyst represent two melting peaks, resulting from catalysis by Cp_2ZrCl_2 and $TiCl_4$, respectively. As shown in Fig. 7(A), the polymer produced on the hybrid catalysts gives bimodal peaks which partly overlap the region of the metallocene catalyst and partly that of the Ziegler-Natta catalyst, suggesting that the polymer is composed of two lamella structures, each of which is polymerized by one of the catalysts. In this case, the polyethylene portion produced by the Ziegler-Natta catalyst is more dominant than that by the metallocene catalyst. This is due to the higher activity of the Ziegler-Natta catalyst vis-à-vis that of the metallocene catalyst over the recrystallized $MgCl_2$.

GPC analysis indicates that the molecular weight increases and the molecular weight distribution is broadened from metallocene to Ziegler-Natta catalyst because the Ziegler-Natta catalyst has the characteristics to produce the high molecular weight polyethylene (long chain polyethylene) and the irregular polymer chains (broad MWD). Particularly, when the molecular weight and the molecular weight distribution of the polymer produced by the homogeneous metallocene catalyst were compared with those by the metallocene supported catalyst, the molecular weight increased and the molecular weight distribution was slightly broadened from the homogeneous to the supported metallocene catalyst. The main reason for this behavior is that the growing polymer chains produced by the metallocene supported catalyst were polymerized over the supports, and as a result, the growing polymers replicate the shape of the supports, thus giving a higher molecular weight and different polymer chains. [Kaminsky and Scheirs, 2000].

The variation of GPC profiles is similar to that of the DSC thermograms, as shown in Fig. 7(B). The molecular weight distribution of polyethylene produced on the hybrid catalyst exhibits a bimo-

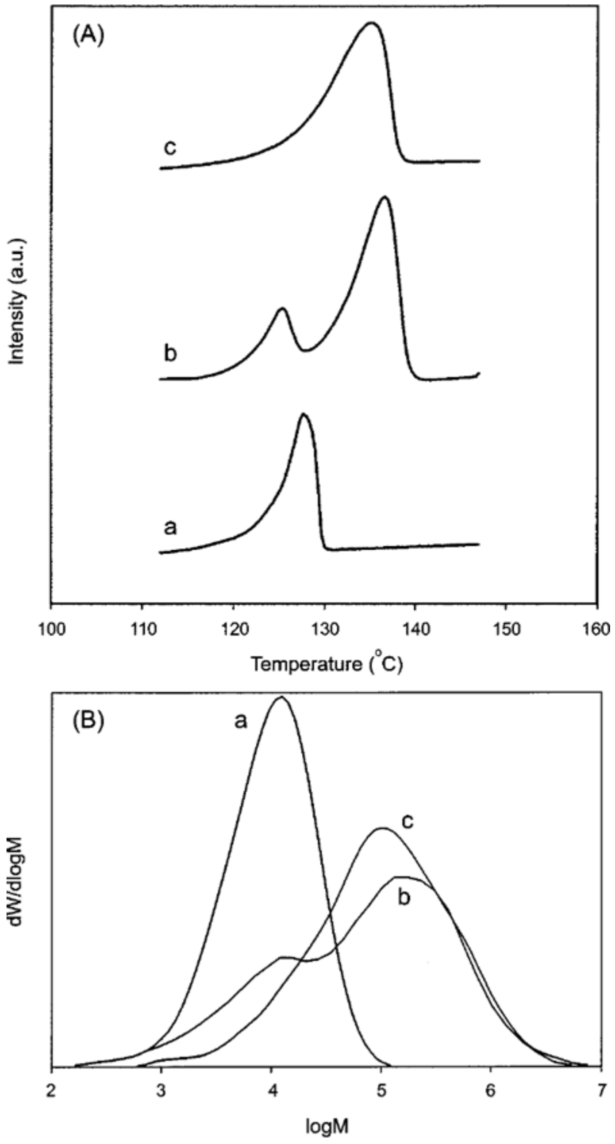

Fig. 7. DSC thermograms and GPC profiles of polyethylene produced by various supported catalysts.
(a) Cp_2ZrCl_2/TIBAL/$MgCl_2 \cdot 4CH_3OH$, MAO (Al/Zr=3000), (b) $TiCl_4$/Cp_2ZrCl_2/TIBAL/$MgCl_2 \cdot 4CH_3OH$, MAO (Al/Zr=3000), (c) $TiCl_4$/TIBAL/$MgCl_2 \cdot 4CH_3OH$, TEA (Al/Ti=300)

dal pattern. One peak in the low molecular weight region was the result from Cp_2ZrCl_2, and the other peak of high molecular weight region from $TiCl_4$. Moreover, the position of the two peaks is coincident with that of the individual polyethylene peak produced by the metallocene and Ziegler-Natta catalyst, respectively. This suggests that the hybrid catalysts acted as individual active species on the support, and that there is no strong chemical interaction between the two catalysts.

CONCLUSIONS

A recrystallized $MgCl_2$ support was prepared by using an alcohol as the dissolution material. The contents of methanol and methoxy in the support are an important factor in hybrid catalyst impregnation. In terms of the treatment of the prepared support, TIBAL was an excellent pretreatment material. The produced polymer showed two different melting points, suggesting that the hybrid catalysts acted as individual active species on the supports. GPC analysis indicated that the molecular weight and molecular weight distribution of polymers produced by the hybrid catalysts were higher and broader than any other polymers for the ethylene polymerization. Consequently, both catalysts appear to be compatible on recrystallized $MgCl_2$ and produce a blend of polymers.

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This paper is dedicated to Prof. Wha Young Lee in honor of his retirement.

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