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The Characteristics of Metallocene/Ziegler-Natta Hybrid Catalysts Supported on the Recrystallized $MgCl_2$

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Abstract–A metallocene catalyst or a metallocene/Ziegler-Natta hybrid catalyst supported on $MgCl_2$ was studied for application to the commercial slurry phase process and to the control of MWD of the polymer produced. The $MgCl_2$ support was prepared by the recrystallization method with different solvents: alcohols and H_2O. The recrystallized $MgCl_2$ support was pretreated with triisobutylaluminum (TiBAL) or trimethylaluminum (TMA), methylaluminoxane (MAO), to give different supporting environments. Metallocene/Ziegler-Natta hybrid catalysts on $MgCl_2$ were prepared by first supporting the metallocene catalyst, followed by the Ziegler-Natta catalyst after pretreatment with an alkylaluminum compound. The type of solvent plays a role in providing a suitable environment in the support for impregnating catalysts. The hybrid catalyst, whose support was recrystallized in n-propanol (n-PrOH) and pretreated with TiBAL, showed the highest molar ratio of Zr/Ti=1/2.71. But the hybrid catalyst, whose support was recrystallized in H_2O and pretreated with MAO, showed the best hybrid effect showing a variety of bimodal peaks in proportion to the ratio of MAO/TEA in GPC analysis. This effect might be due to steric factor and polarity of solvent, as well as the pretreatment material. It is concluded that the MWD of polyethylene produced by metallocene/Ziegler-Natta hybrid catalyst that is supported on $MgCl_2$ can be controlled by regulating the amounts of MAO and TEA added as cocatalysts and by the use of different solvents and pretreatment materials.

Key words : Recrystallized $MgCl_2$, Solvent, Pretreatment Material, Metallocene/Ziegler-Natta Hybrid Catalyst, Ethylene Polymerization, Hybrid Effect

INTRODUCTION

Metallocene catalyst systems, discovered by Kaminsky and Sinn in the early 1980's, have become the next generation catalysts for olefin polymerization. Such systems show a high activity for olefin polymerization and are capable of producing polymers with special properties which are unattainable via Ziegler-Natta catalyst systems [Yoon et al., 1996; Zambelli et al., 1991]. As a result, numerous studies, both industrial and academic, have been done. The metallocene catalyst systems are basically homogeneous systems, and the majority of studies on such catalysts have concentrated on solution-phase processes. However, in order for metallocene catalysts to be used in the prevailing slurry or gas phase processes, a supported metallocene catalyst is essential. In addition, since all commercial polymerization processes using Ziegler-Natta catalysts are heterogeneous systems, the preparation of the heterogeneous metallocene catalysts is a prerequisite for the existing processes. In recent studies, a variety of supports such as SiO_2 [Soga and Kaminaka, 1992], Al_2O_3 [Soga and Kaminaka, 1994], zeolite [Woo et al., 1996], etc. have been used. Although metallocene catalysts have the advantages of high activity and special polymer properties, the polymers produced in homogeneous systems have a very narrow molecular weight distribution (MWD, M_w/M_n). In polymer processing, molecular weight and MWD are important because they determine both mechanical and rheological properties. On the one hand, polyethylenes with narrow MWD lead to products with higher impact resistance and higher resistance to environmental stress-cracking. On the other hand, polyethylenes with a broad MWD show greater flowability in the molten state at high shear rate, which is important for blowing and extrusion techniques [Ahlers and Kaminsky, 1988]. Therefore, it is possible that the narrow MWD via metallocene catalysts could be broadened by preparing Ziegler-Natta/Metallocene hybrid catalysts because of the relatively higher molecular weight of polymers produced by the Ziegler-Natta catalyst fraction. Hybrid catalysts can take advantage of the properties of both the metallocene and Ziegler-Natta catalysts. In addition, hybrid catalysts would be expected to be utilized in prevailing processes without significant process modification and to enhance processability of the polymers. In this study, $MgCl_2$ prepared by a recrystallization method using methanol solvent was utilized as a support. The new type of hybrid catalysts was prepared for the polymerization of ethylene. The prepared supports and the hybrid catalysts were characterized by ICP, TGA. Ethylene monomer was polymerized in order to investigate the characteristics of the hybrid catalysts.

EXPERIMENTAL

1. Materials

Nitrogen of high purity and ethylene (Sinyang Gas Products) were further purified prior to use by sequentially passing them through columns of 5 Å molecular sieves (Kokusan Chem.), anhydrous P_2O_5 (Yakuri Chem.), and RIDOX, an oxygen scav-

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enger (Fischer Scientific). The molecular sieves were regenerated in every 2 months by treatment with a stream of N_2 at 250 °C, and the oxygen scavenger was activated by treatment with a stream of H_2 at 250 °C. Toluene (Oriental Chem.) that was used as a solvent for the catalyst preparation and for polymerization was purified by distillation over metal sodium under an N_2 atmosphere to remove residual traces of moisture and oxygen. $MgCl_2$ (Aldrich Chem.), CH_3OH (MeOH, Carlo Erba.), C_2H_5OH (EtOH, J. T. Baker), n-C_3H_7OH (n-PrOH, Junsei), Cp_2ZrCl_2 (Strem Chem.), $TiCl_4$ (Aldrich Chem.), triisobutylaluminum (TiBAL, Aldrich Chem.), trimethylaluminum (TMA, Aldrich Chem.), methylaluminoxane (MAO, type 4, Akzo Chem.) were used without further purification.

2. Preparation of Support and Catalyst

Anhydrous $MgCl_2$ (0.1 mol) was introduced into a glass reactor equipped with a magnetic stirrer, and 100 ml of alcohol (methanol, ethanol, n-propanol) or distilled water was added. The mixture of $MgCl_2$ and solvent was heated to 60 °C and stirred until $MgCl_2$ was completely dissolved. Then 100 ml of n-decane (for alcohol dispersion) or corn oil (for water dispersion) was added to this homogeneous solution and the final mixture was stirred at 2,000 rpm under vacuum at 80 °C or 100 °C. Next, $MgCl_2$ particles of spherical shape were slowly precipitated in n-decane or corn oil medium, as the solvent evaporated. The resulting $MgCl_2$ particles were washed four times with toluene to remove residual n-decane or corn oil and then dried under vacuum to remove toluene. Thus the recrystallized $MgCl_2$ was obtained. Also, thermally treated $MgCl_2$ support which was recrystallized with H_2O was attained by heating at 100 °C for 15 minutes or 200 °C for 2 hrs, denoted as $H_2O/MgCl_2$-100, $H_2O/MgCl_2$-200 respectively. 5 g of support was introduced into a 500 ml flask equipped with a water-cooled reflux condenser and a magnetic stirrer. An equivalent amount of alkylaluminum compound or MAO to the solvent content in the support and 100 ml of toluene as a diluent was then added into the flask. The mixture was stirred at 0, 20, 40, 60 °C for 30 minutes successively and then stirred at 80 °C for two hours to complete the reaction between alkylaluminum and solvent. The mixture was then washed with 100 ml of toluene for 6 times to remove the unreacted alkylaluminum or MAO and finally dried under vacuum to give the alkylaluminum/solvent/$MgCl_2$, or MAO/solvent/$MgCl_2$. The washed supports (2 g) were suspended in 100 ml of toluene and reacted with 0.10 g Cp_2ZrCl_2 at 50 °C for 2 hours and then washed in the same manner. After preparation of this metallocene supported catalyst, 2 ml of $TiCl_4$ was introduced into this catalyst, and the mixture was stirred for two hours at 80 °C. After the reaction, the mixture was washed 6 times with 100 ml of toluene to give the final metallocene/Ziegler-Natta hybrid catalysts. These hybrid catalysts, denoted as $TiCl_4/Cp_2ZrCl_2$/alkylaluminum compound or MAO/solvent/$MgCl_2$, were suspended in 100 ml of toluene and used as catalysts.

3. Characterization

Thermogravimetric analysis (TGA) (TGA 7, Perkin-Elmer) was used to determine the solvent content in the recrystallized $MgCl_2$. The desorbed temperature of the solvent from $MgCl_2$ was measured by differentiating TGA thermogram. An X-ray diffractometer (JDX-5 p, JEOL) was used to determine the crystallinity of recrystallized $MgCl_2$ supports, and the composition of supports was identified from JCPDS Card Index File. The degree of solvent elimination which remained in the recrystallized $MgCl_2$ was confirmed by FT-IR (Impact-410, Nicolet) measurement at each step in the course of preparing hybrid catalyst. Surface area of supports and catalysts was determined by Quantasorb (ASAP 2010, Micromeritics). Scanning Electron Microscopy (SEM) (JSM-35, JEOL) was used to observe the morphology of the support and the catalyst. The titanium and zirconium contents of the catalysts were measured using Inductively Coupled Plasma (ICP) (VG PQ2-Turbo, VG elemental). The Differential Scanning Calorimetry (DSC) (DSC 2010, TA instruments) was carried out 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) at 160 °C with 1,2,4-trichlorobenzene as a solvent.

4. Polymerization of Ethylene

300 ml of toluene and cocatalyst (LAO or alkylaluminum compound) were introduced into a 1 L glass reactor, equipped with a magnetic stirrer under a stream of dry N_2 and then evacuated to remove the N_2. Ethylene and hydrogen was then fed at a constant pressure of 1.3 bar and 0.2 bar, respectively. The polymerization was initiated by introducing the catalyst suspension into the reactor with a syringe. After 50 minutes, polymerization reaction was stopped by adding a solution composed of a dilute hydrochloric acid and methanol into the reactor. Then, the polymer was separated and dried. The polymerization rate was determined by measuring the amount of consumed ethylene with a mass flowmeter.

RESULTS AND DISCUSSION

It is well known that if metallocene is directly impregnated on a support in the absence of any surface modification, both the degree of impregnation and the catalytic activity are usually low [Soga and Kaminaka, 1992]. It is also known that the Ziegler-Natta catalyst has more affinity for a $MgCl_2$ support than metallocene. Therefore, if $MgCl_2$ is utilized as a support, the amount of impregnated zirconocene and its activity are more important to the catalyst system than that of Ziegler-Natta catalyst. In this study, the $MgCl_2$ support was prepared by a recrystallization method developed in our laboratory [Park and Lee, 1992]. Alcohol or water was used as solvent and, of the alcohols available, only MeOH, EtOH and n-PrOH could dissolve $MgCl_2$. Thus, steric hindrance might be a factor in this system. Since alcohol and water are Lewis bases, they act as deactivators of the metallocene catalyst and, as such, should be eliminated or reduced to the lowest possible level. Two methods have been used to accomplish this. The first one involves physically heating under an N_2 atmosphere to reduce the level of solvent, and the second one is a chemical reaction between the solvent and an alkylaluminum compound such as TMA, TiBAL, or MAO. Supports prepared using these methods resulted in a different $MgCl_2$ surface and, as a result, different environments for catalyst impregnation. Consequently, the influence on the respective activity of metallocene and the Zie-

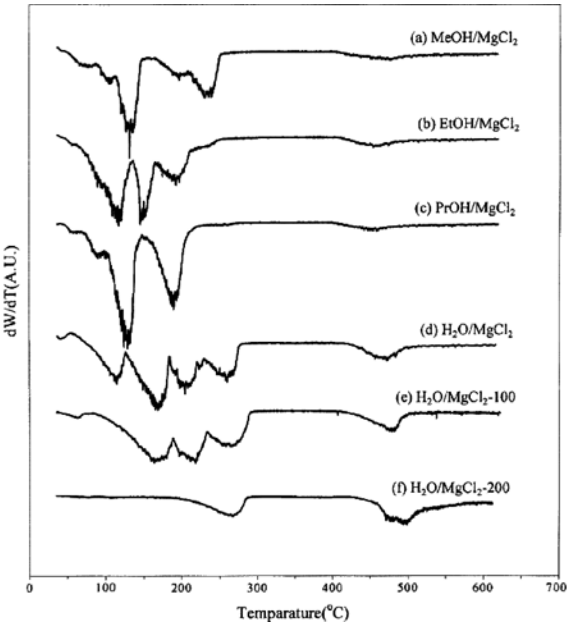


Fig. 1. DTG thermograms of the recrystallized $MgCl_2$ in various solvents.

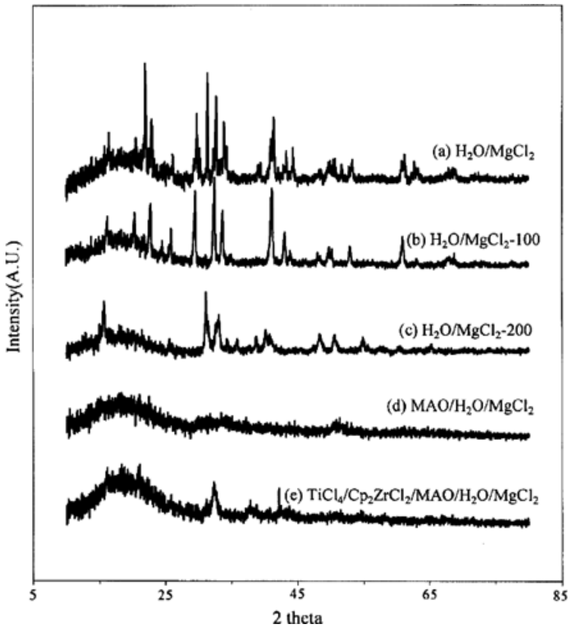


Fig. 2. XRD patterns of the recrystallized $MgCl_2$ supports and catalysts.

gler-Natta catalyst might be different and the characteristics of polymers produced on each catalyst might also be different.

1. Characterization of the Recrystallized $MgCl_2$

In order to investigate the binding state of solvents to $MgCl_2$ supports, we analyzed the recrystallized $MgCl_2$ in different solvents by DTG, as shown in Fig. 1. The weight reduction of supports during the slow heating up to 650 °C was calculated using TGA curves and is listed in Table 1. In the case of $H_2O/MgCl_2$ support, the extent of weight reduction reached 65.4% as shown in Table 1. Since $MgCl_2$ itself decomposes at temparatures above 300 °C, the weight reduction below 300 °C is assumed to be the result of the desorption of H_2O which remains in the $MgCl_2$ as combined water in the form of $MgCl_2 \cdot nH_2O$. The $H_2O/MgCl_2$ support has been reported to be decomposed as shown below [Bart and Roovers, 1995].

$$\begin{aligned} MgCl_2\cdot 6H_2O &\xrightarrow{117\text{-}160^\circ C} MgCl_2\cdot 2H_2O \\ &\xrightarrow{190^\circ C} MgCl_2\cdot 2H_2O \\ &\xrightarrow{240^\circ C} MgCl_2\cdot H_2O \\ &\xrightarrow{285^\circ C} Mg(OH)Cl \\ &\xrightarrow{520^\circ C} MgCl_2 + MgO \end{aligned}$$

According to the above scheme, the weight reduction of $MgCl_2\cdot 6H_2O$ is calculated to be 66.7%. Therefore, 65.4% weight reduction of $H_2O/MgCl_2$ support is equivalent to $MgCl_2\cdot 5.59H_2O$. Anhydrous $MgCl_2$ exhibits a cubic closest packing (ccp) structure giving strong reflection patterns at $2\theta=35°$ (004 plane), 15° (003 plane) and 50° (110 plane) [Magalhaes et al., 1991]. However, in the XRD pattern of $H_2O/MgCl_2$, all reflections at 35°, 15° and 50° disappeared and other reflections of new shapes and different strengths appeared at new positions, as shown in Fig. 2(a). The XRD pattern of $H_2O/MgCl_2$ can be found in the previously reported XRD pattern of $MgCl_2\cdot 6H_2O$ [ICDD PDF No 25-0515] at $2\theta=21.6°$, 31.0°, 33.8° for major peaks and $MgCl_2\cdot 4H_2O$ [ICDD PDF No 01-1210] at $2\theta=29.6°$, 32.5°, 41.0° for minor peaks. The relative intensities of these peaks were affected by the vacuum drying time during the recrystallization process. In addition, Park and Lee [Park and Lee, 1992] reported that $EtOH/MgCl_2$ was formed from $MgCl_2\cdot 6H_2O$ to be $MgCl_2\cdot 6EtOH$ by activation by the recrystallization method. Alcohol/$MgCl_2$ supports can be regarded as $MgCl_2\cdot$n(alcohol). From the DTG (Fig. 1), XRD (Fig. 2), and previous reports, it is concluded that $MgCl_2$ supports, which are recrystallized from various alcohols or water, exist in the form of $MgCl_2\cdot$n(alcohol or H_2O).

Table 1. Contents of various solvents remaining in $MgCl_2$ after recrystallization

Recrystallizing solvent	MeOH	EtOH	PrOH	H_2O	H_2O-100	H_2O-200
Reduced weight %	60.5	62.8	72.9	65.4	59.2	41.5

Two types of supports were also prepared by the thermal treatment of $H_2O/MgCl_2$. The $H_2O/MgCl_2$-100 support was prepared by physical heating of $H_2O/MgCl_2$ at 100 °C for 15 minutes and $H_2O/MgCl_2$-200 support at 200 °C for 2 hrs. The DTG thermogram in Fig. 1(e), (f) shows that a smaller amount of H_2O is desorbed from $H_2O/MgCl_2$-100 and $H_2O/MgCl_2$-200 than from $H_2O/MgCl_2$ at the low temperature range. Since the weight reduction of $H_2O/MgCl_2$-100 support is 59.2%, it can be regarded as being $MgCl_2\cdot 3.94H_2O$, and the 41.5% weight reduction of $H_2O/MgCl_2$-200 can be designated as $MgCl_2\cdot 1.14H_2O$. The XRD pattern of $H_2O/MgCl_2$-100 support in Fig. 2(b) corresponds to $MgCl_2\cdot 4H_2O$ [ICDD PDF No 01-1210] and that of the $H_2O/MgCl_2$-200 support in Fig. 2(c) is consistent with the previously reported XRD pattern of $MgCl_2\cdot H_2O$ [ICDD PDF No 01-0947].

2. Effect of Pretreatment of Support on Impregnating Catalyst

Since alcohol or water acts as a deactivation material for the metallocene catalyst, the recrystallized $MgCl_2$ was treated with alkylaluminum compounds such as TMA, TiBAL, or MAO to eliminate any remaining alcohol or water. To determine the optimum amount of pretreatment material, different amounts of TiBAL, such as 1, 0.75, 0.50, 0.25 mol ratio of TiBAL/MeOH content in the MeOH/$MgCl_2$ support, was introduced to the support, followed by impregnation of Cp_2ZrCl_2, as shown in Table 2. The above catalysts were denoted as Cp_2ZrCl_2/TiBAL (mol ratio of TiBAL/MeOH content)/MeOH/$MgCl_2$. It was found that the amount of impregnated Cp_2ZrCl_2 and the activity of polymerization were proportional to the amount of the pretreatment material, TiBAL. In particular, Cp_2ZrCl_2/TiBAL(1)/MeOH/$MgCl_2$ showed large difference in activity from the three other catalysts. Only slight differences among Cp_2ZrCl_2/TiBAL (0.75)/MeOH/$MgCl_2$, Cp_2ZrCl_2/TiBAL(0.5)/MeOH/$MgCl_2$ and Cp_2ZrCl_2/TiBAL(0.25)/MeOH/$MgCl_2$ were observed. This suggests that the sites formed by the reaction between the solvent and the alkylaluminum compound are effective for the impregnation of Cp_2ZrCl_2, and that the MeOH which remained in the $MgCl_2$ after TiBAL treatment acted as a deactivating source for Cp_2ZrCl_2. Accordingly, it can be concluded that an amount of pretreatment material sufficient to eliminate the solvent is essential for effective impregnation and a high activity of Cp_2ZrCl_2.

Table 2. Effect of pretreatment with respect to the amount of TiBAL on Cp_2ZrCl_2 impregnation

Catalyst	Zr (wt%)	Activity**
Cp_2ZrCl_2/TiBAL(1)*/MeOH/$MgCl_2$	1.11	47.4
Cp_2ZrCl_2/TiBAL(0.75)*/MeOH/$MgCl_2$	0.108	7.1
Cp_2ZrCl_2/TiBAL(0.5)*/MeOH/$MgCl_2$	0.090	trace
Cp_2ZrCl_2/TiBAL(0.25)*/MeOH/$MgCl_2$	0.027	trace

*amount of treated TiBAL, unit : mol ratio of TiBAL/MeOH content

**unit : kg-PE/g-Zr.bar.hr

Polym'n condition: T_p=70 °C, $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, MAO/Zr=1000, diluent=toluene.

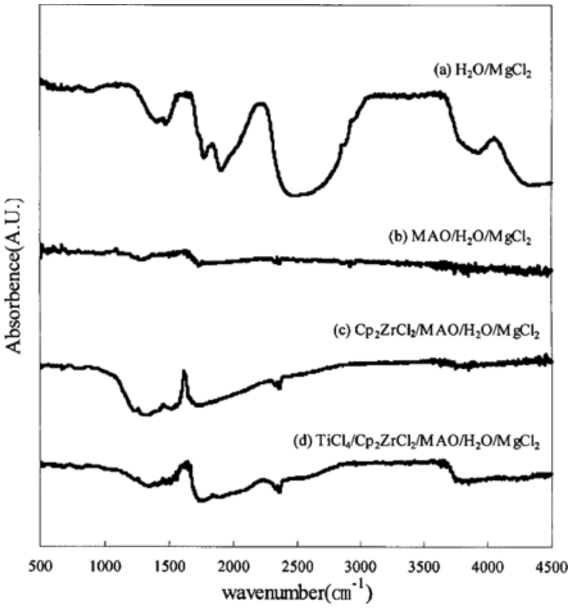


Fig. 3. IR spectra of the recrystallized $MgCl_2$ support and catalysts.

To study the character of the site where the solvent and alkylaluminum reacted, XRD and IR methods were utilized. The XRD pattern in Fig. 2(d) showed no reflections when the H_2O/$MgCl_2$ support was treated with MAO, indicating that MAO/H_2O/$MgCl_2$ does not form a crystal. On the other hand, in comparing IR data of Fig. 3(a) and Fig. 3(b), it was found that the H_2O peak of H_2O/$MgCl_2$ in the range of 3,000 cm^{-1} to 3,700 cm^{-1} in Fig. 3(a) had completely disappeared after treatment with MAO, as shown in Fig. 3(b). These results suggest that water of H_2O/$MgCl_2$ had completely reacted with MAO to form a complex. Chien and coworkers suggested a mechanism in which Si-O-Al formed on the surface of silica by the reaction of Si and MAO can produce zirconocene methyl cation species by eliminating Cl^- from zirconocene [Chien and He, 1991]. Soga suggested that MAO is anchored to the hydroxyl groups (-OH) present on the surface of the SiO_2 support and that this anchored MAO reacts with another MAO which is combined to the zirconocene to form the active species [Soga and Kaminaka, 1993]. The above results and previous reports suggest that the alkylaluminum compound (MAO) is combined to the hydroxyl group of alcohol or the water present in recrystallized $MgCl_2$ to form Mg-O-(MAO) followed by a reaction with zirconocene to form the active cationic species.

The amount of alkylaluminum required is equivalent to the moles of alcohol or water in the support. Even for the case of the thermally treated support, all alkylaluminum compound should be added to treat the solvent remaining in the support. In this case, however, only a small amount of alkylaluminum compound is needed, because the content of the remaining water is small. To investigate the influence of water content present in a support on the amount of zirconocene impregnated and the catalytic activity, MAO was used to treat three different supports such as H_2O/$MgCl_2$, H_2O/$MgCl_2$-100, and H_2O/Mg-Cl_2-200. Table 3 shows the content of aluminum and zirconium in the catalysts as analyzed by ICP and the activity of catalysts. Of course the Al content increased with the amount of MAO introduced. The amount of impregnated zirconocene and the activity increased with the aluminum content, but the difference of activity was not so high as the results in Table 2. Since no additional water remaines in MAO/H_2O/$MgCl_2$-100 and MAO/H_2O/$MgCl_2$-200 after treatment with alkylaluminum, no big difference in activity among the thermally treated catalysts was observed. In

Table 3. Elemental analysis of catalysts on thermally non-treated and treated supports

Catalyst	Al (wt%)	Zr (wt%)	Activity*
Cp_2ZrCl_2/MAO/H_2O/$MgCl_2$	28.6	1.30	14.4
Cp_2ZrCl_2/MAO/H_2O/$MgCl_2$-100	8.10	0.46	11.7
Cp_2ZrCl_2/MAO/H_2O/$MgCl_2$-200	2.44	0.34	7.5

*unit : kg-PE/g-Zr.bar.hr

Polym'n condition: T_p=70 °C, $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, MAO/Zr=1000, diluent=toluene.

order for the active metallocene species to be impregnated on the recrystallized $MgCl_2$, sufficient sites formed by the reaction of H_2O residues and the use of a stoichiometric amount of MAO is desireable. The thermally treated supports do not provide a favorable environment for the impregnation of zirconocene. In this respect, the supports that are not thermally treated were the object of our attention.

3. Effect of Solvent and Alkylaluminum Compound on Catalyst Impregnation

To study the influence of solvents and alkylaluminum compounds on catalyst impregnation, Cp_2ZrCl_2 initially, and then $TiCl_4$ were impregnated on the various supports prepared under different conditions and the content of Zr and Ti was analyzed by ICP, as shown in Table 4. It has been reported that TiBAL among TiBAL, TEA and HMDS were shown to be the most effective as a pretreatment material for zirconocene impregnation on the MeOH/$MgCl_2$ support and also good activity [Cho et al., 1998]. Thus, TiBAL and MAO, in addition, were select-

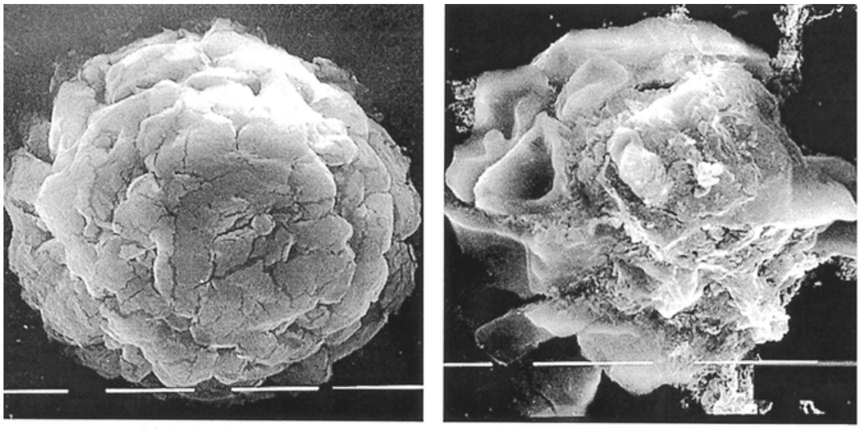
Table 4. ICP results for various solvents and pretreatment materials

	Catalyst	Zr (wt%)	Ti (wt%)	Activity**
(a)	$TiCl_4/Cp_2ZrCl_2$/TiBAL/MeOH/$MgCl_2$	0.97	2.09	31.8
	$TiCl_4/Cp_2ZrCl_2$/TEA/MeOH/$MgCl_2$*	0.051	3.85	25.8
	$TiCl_4/Cp_2ZrCl_2$/MAO/MeOH/$MgCl_2$	0.20	3.09	4.9
(b)	$TiCl_4/Cp_2ZrCl_2$/TiBAL/MeOH/$MgCl_2$	0.97	2.09	31.8
	$TiCl_4/Cp_2ZrCl_2$/TiBAL/EtOH/$MgCl_2$	0.76	1.68	9.4
[CAT1]	$TiCl_4/Cp_2ZrCl_2$/TiBAL/PrOH/$MgCl_2$	1.00	1.42	11.8
	$TiCl_4/Cp_2ZrCl_2$/TiBAL/H_2O/$MgCl_2$	0.52	2.68	4.9
(c)	$TiCl_4/Cp_2ZrCl_2$/TiBAL/H_2O/$MgCl_2$	0.52	2.68	4.9
	$TiCl_4/Cp_2ZrCl_2$/TMA/H_2O/$MgCl_2$	trace	2.10	11.8
[CAT2]	$TiCl_4/Cp_2ZrCl_2$/MAO/H_2O/$MgCl_2$	0.83	4.33	1.5

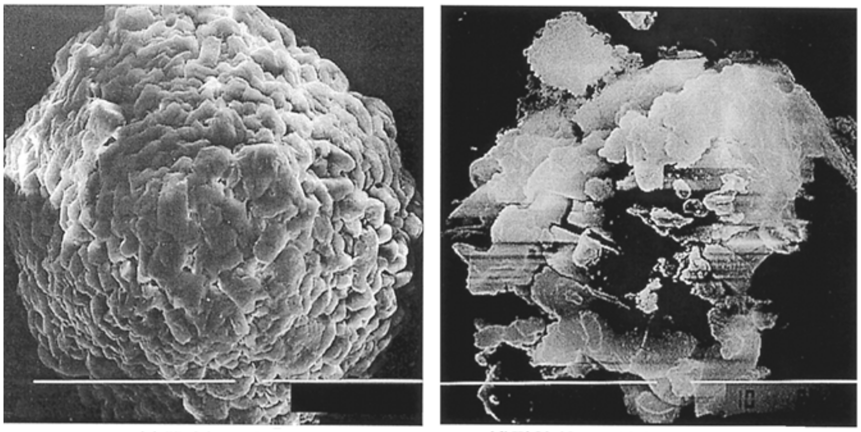
*sited in ref. [Cho et al., 1998]

**unit : kg-PE/g-Mt.bar.hr

Polym'n condition: T_p=70 °C, $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, MAO/Zr=1,000, diluent=toluene.



(a) PrOH/$MgCl_2$ (b) $TiCl_4/Cp_2ZrCl_2$/TiBAL/PrOH/$MgCl_2$



(c) H_2O/$MgCl_2$ (d)$TiCl_4/Cp_2ZrCl_2$/MAO/H_2O/$MgCl_2$

Fig. 4. SEM images of the recrystallized $MgCl_2$ supports and catalysts.

ed as pretreatment materials in this study. However, TiBAL proved to be superior to MAO, for pretreatment, as shown in Table 4(a). Therefore, TiBAL was used as a pretreatment material for all the alcohol/$MgCl_2$ supports. As shown in Table 4(b), the largest amount of Cp_2ZrCl_2 and the least amount of $TiCl_4$ were impregnated when n-PrOH was used as a solvent for $MgCl_2$. With respect to the hybrid effect, it would be expected that $TiCl_4$/Cp_2ZrCl_2/TiBAL/PrOH/$MgCl_2$ would have the best effect among the catalysts tested, if all the impregnated catalysts are active and not deactivated. These results suggest that the molecular sizes of solvents and the alkylaluminum compound play a role in providing zirconocene impregnation. Pr-OH and TiBAL of which the molecule sizes are bulky might be used to prepare more sites and more porous sites with good environments for the zirconocene impregnation. Because of the preoccupation by the zirconocenes on $MgCl_2$ support, fewer sites remained for $TiCl_4$ impregnation. In order to investigate the proper alkylaluminum compound for zirconocene impregnation on H_2O/$MgCl_2$, three types of alkylaluminum compounds were tested as shown in Table 4(c). Zirconocene was impregnated well on the support treated with MAO, which is different from the results for alcohol/$MgCl_2$ supports. This result may be attributed to the stable combination of the zirconocene cation on MAO anchored on $MgCl_2$ support. The stable combination of MAO on $MgCl_2$ is caused by the property of MAO as a moisture scavenger and by the stronger polarity of H_2O than alcohol. Actually, when MAO was injected to the H_2O/$MgCl_2$ support, a strong exothermic reaction was observed. This suggests that MAO was strongly combined to H_2O present in the support, resulting in a good environment for the impregnation of the zirconocene. The catalyst activity will be discussed in a later section.

4. Morphology of Supports and Catalysts

Fig. 4 shows SEM photographs of supports and hybrid catalysts. Since the supports are prepared by a recrystallization method, the shape of PrOH/$MgCl_2$ and H_2O/$MgCl_2$ supports shows a spherical morphology which is the same as that of the MeOH/$MgCl_2$ support in our previous reports [Cho et al., 1998; Chung et al., 1995]. The surface area of anhydrous $MgCl_2$ was about 1.15 m^2/g. However, that of the recrystallized $MgCl_2$ increased up to about 20 m^2/g. The morphology of the impregnated Cp_2ZrCl_2 was not changed, suggesting an ionic interaction of Cp_2ZrCl_2 with the alkylaluminum compound and no reaction of Cp_2ZrCl_2 with $MgCl_2$. However, when $TiCl_4$ was impregnated, the catalyst became more porous, suggesting that there was a vigorous reaction between $MgCl_2$ and $TiCl_4$ to lead a direct binding of $TiCl_4$ to $MgCl_2$. These results provide support for the fact that the Ziegler-Natta catalyst has more affinity for $MgCl_2$ than metallocene.

5. Polymerization of Ethylene

The characteristics of polyethylenes produced by the hybrid catalysts, which were prepared by the successive impregnation of Cp_2ZrCl_2 and $TiCl_4$ on the (alcohol or H_2O)/$MgCl_2$ support after pretreatment with the alkylaluminum, were investigated as a function of different amounts of TEA and MAO, as shown in Table 5. And the most promising catalysts, $TiCl_4$/Cp_2ZrCl_2/TiBAL/PrOH/$MgCl_2$ and $TiCl_4$/Cp_2ZrCl_2/MAO/H_2O/$MgCl_2$, were selected, denoted as CAT1 and CAT2, respectively. The activity of both catalysts decreased with increasing TEA/Ti ratios. This is due to the fact that TEA acts as a deactivating material

Table 5. The characteristics of the produced PE with respect to the amount of cocatalysts on hybrid catalyst systems

Catalyst	Cocatalyst molar ratio	Activity*	T_m (°C)	M_w ($\times 10^{-5}$)	MWD
[CAT1]	MAO/Zr=1000	11.8	131.04	6.47	13.3
$TiCl_4$/Cp_2ZrCl_2/			136.15		
TiBAL/PrOH/$MgCl_2$	MAO/Zr=1000	10.1	131.03	7.35	16.4
	TEA/Ti=25		136.25		
	MAO/Zr=1000	7.5	129.09	7.45	8.82
	TEA/Ti=50		136.70		
(Zr=1.00 wt%	MAO/Zr=1000	5.0	130.00	6.91	9.53
Tr=1.42 wt%	TEA/Ti=100		139.03		
Zr/Ti=1/2.71)	TEA/Ti=100	4.9	138.38	6.97	7.01
[CAT2]	MAO/Zr=1000	1.5	132.28	6.20	19.4
$TiCl_4$/Cp_2ZrCl_2/			139.82		
MAO/H_2O/$MgCl_2$	MAO/Zr=10000	0.5	130.27	13.0	23.2
	TEA/Ti=25		140.36		
	MAO/Zr=1000	0.5	140.46	-**	-**
	TEA/Ti=50				
(Zr=0.83 wt%	MAO/Zr=1000	0.5	140.18	-**	-**
Tr=4.33 wt%	TEA/Ti=100				
Zr/Ti=1/9.94)	TEA/Ti=100	0.6	141.13	21.5	11.1

*Activity : kg-PE/g-Mt.bar.hr

**Could not be measured because of being not dissolved in TCB solution.

Polym'n condition: T_p=70 °C, $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, diluent=toluene.

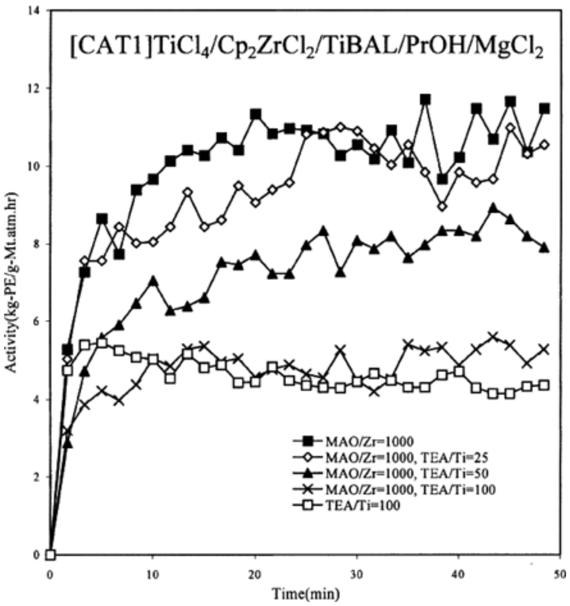


Fig. 5. Activity profiles for ethylene polymerization over $TiCl_4$/Cp_2ZrCl_2/TiBAL/PrOH/$MgCl_2$.
Polym'n condition : T_p=70 °C ; $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, Polym'n time=50 min, diluent=toluene

Table 6. The characteristics of PE produced by various Cp_2ZrCl_2 catalyst systems

	Catalyst	Activity*	T_m (°C)	M_w ($\times 10^{-5}$)	MWD
	Cp_2ZrCl_2	51.0	127.0	0.111	1.89
[CAT1]	Cp_2ZrCl_2/TiBAL/PrOH/$MgCl_2$	45.9	133.9	0.979	4.94
	$TiCl_4$/Cp_2ZrCl_2/TiBAL/PrOH/$MgCl_2$	11.8	136.2	6.47	13.3
	$TiCl_4$/TiBAL/PrOH/$MgCl_2$	7.8	137.1	-**	-**
[CAT2]	Cp_2ZrCl_2/MAO/H_2O/$MgCl_2$	14.4	130.4	0.329	26.7
	$TiCl_4$/Cp_2ZrCl_2/MAO/H_2O/$MgCl_2$	1.5	132.3 139.8	6.20	19.4
	$TiCl_4$/MAO/H_2O/$MgCl_2$	3.2	143.0	16.0	12.5

*Activity : kg-PE/g-Mt.bar.hr

**could not be measured because of insolubility in the TCB solution.

Polym'n condition: T_p=70 °C, $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, diluent=toluene, MAO/Zr=1,000 (for $TiCl_4$-supported catalyst, MAD/Ti=1000)

for the active zirconocene species. Fig. 5 shows the activity profile of CAT1. In the case of a $MgCl_2$-supported Ziegler-Natta catalyst [Guyot et al., 1987] and a homogeneous metallocene catalyst, the activities decrease with reaction time. However, the activity of CAT1 remained constant during polymerization for a period of 50 minutes. This suggests that the impregnated active zirconocene species were well dispersed and, accordingly, the $TiCl_4$ which was impregnated over the impregnated zirconocene was also well dispersed. The activities of all other catalysts remained constant. In order to confirm that Cp_2ZrCl_2 and $TiCl_4$ were successfully impregnated on $MgCl_2$ support and do not exist in toluene as homogeneous catalysts, a small amount of toluene in the catalyst flask was injected during the polymerization. No change in activity was observed. This suggests that Cp_2ZrCl_2 and $TiCl_4$ were successfully impregnated. The T_m difference between polyethylenes produced by homogeneous Cp_2ZrCl_2 and by $MgCl_2$-supported Cp_2ZrCl_2, as shown in Table 6 also confirms this. Fig. 6 shows the thermal analysis of polyethylene produced by CAT1 and CAT2. Generally, the melting temperature (T_m) of a polymer increases with its molecular weight (MW). In Fig. 6, the melting temperature of polymers is closely related to the type of cocatalyst and the molar ratio of cocatalyst to zirconocene and $TiCl_4$. When the molar ratio of MAO/Zr was 1000, polyethylene showed two different melting temperatures. However, when another cocatalyst, TEA was added in the molar ratio of TEA/Ti from 25 to 100, along with MAO and zirconocene in the molar ratio of MAO/Zr=1000, the low melting temperature peak was gradually reduced and finally disappeared and only the high melting temperature peak remaining. The T_m peak around 130 °C corresponds to the lower MW polymer synthesized on the zirconocene site, and the T_m peak around 140 °C represents the higher MW polymer formed on the $TiCl_4$ site. The decrease in the T_m peak intensity around 130 °C suggests the deactivation of the metallocene site. The bimodal peaks partly overlap the regions of a high melting temperature peak and a low melting temperature peak. This suggests that this polymer is composed of two lamella structures which are polymerized by each of the catalysts, respectively. Comparing the intensities of the two bimodal peaks corresponding to CAT1 and CAT2 in Fig. 6, we can see that the low T_m peak, which corresponds to a polyethylene produced on zirconocene sites on CAT2, is higher than that produced on CAT1. This suggests that for the case of CAT2, the zirconocene sites are relatively more active than $TiCl_4$ and for the case of CAT1, the relative activity is reversed. However, comparing the activities of CAT1 and CAT2 in Table 5, the total activity of CAT1 is much higher than that of CAT2. Integrating the results in Table 5 and Fig. 6, the activity of $TiCl_4$ on CAT2 is extremely low, considering that the amount of $TiCl_4$ impregnated on CAT2 is 3 times that on CAT1. This supports the conclusion that most of the $TiCl_4$ on CAT2 had reacted with water present in $MgCl_2$ to form inactive Ti compounds. GPC chromatograms

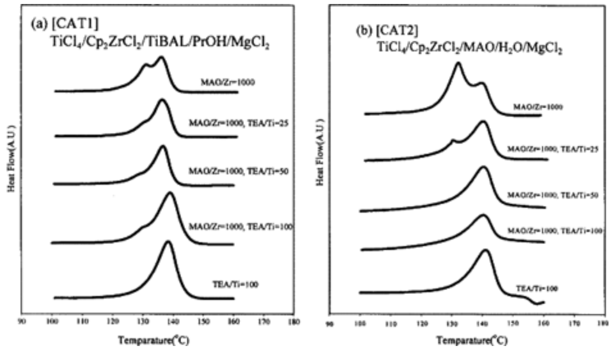


Fig. 6. DSC thermograms of PE produced by hybrid catalysts.
Polym'n condition : T_p=70 °C ; $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, Polym'n time=50 min, diluent=toluene

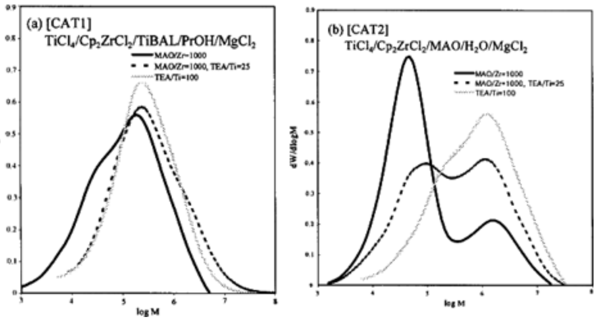


Fig. 7. The molecular weight distributions of PE produced by hybrid catalysts.
Polym'n condition : T_p=70 °C ; $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, Polym'n time=50 min, diluent=toluene

in Fig. 7 show the same results as DSC curves. All GPC curves for PE produced by CAT1 exhibited a wide MWD with a shoulder peak in the condition of MAO/Zr=1000. But as the TEA increased, the shoulder peaks disappeared. CAT2 exhibited a clearer hybrid effect showing evident inversion of bimodal peak intensity with an increase in the TEA/Ti molar ratio. The MW and molecular weight distribution (MWD) were considerably changed depending on the amount of TEA. This result indicates that MWD can be controlled by appropriate adjustment of the molar ratio of TEA/Ti.

In order to study the influence of catalyst impregnation on the characteristics of polyethylene, the polymerization for ethylene was conducted with the homogeneous metallocene (Cp_2ZrCl_2), the supported metallocene catalyst, the hybrid catalyst, and the supported Zigler-Natta catalyst. The experimental results are shown in Table 5 and Fig. 8. The activity decreased with the amount of Ziegler-Natta catalyst, due to the low activity of $TiCl_4$, compared with that of Cp_2ZrCl_2. Fig. 8 shows the MW and MWD of polyethylene produced from four different catalyst systems. Comparing the polyethylene from the supported metallocene catalyst with that from the homogeneous metallocene, no large difference, but only slight shift in MW, was observed. The MWD was narrow due to a single active site of Cp_2ZrCl_2. However, both the MW and MWD of polyethylene from the hybrid catalyst increased drastically. This is due to the fact that two types of polymers are formed on the hybrid catalyst. For the case of $MgCl_2$-supported Ziegler-Natta catalyst, polyethylene with a large MW and MWD were produced, due to the multi active sites of $TiCl_4$.

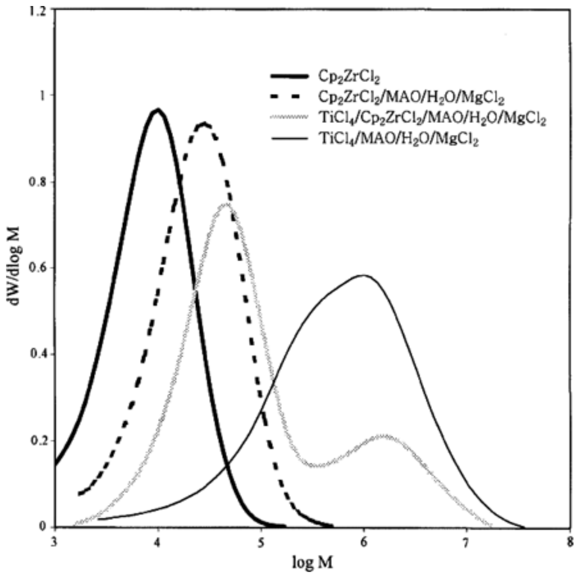


Fig. 8. The molecular weight distributions of PE produced by Cp_2ZrCl_2 catalyst system.
Polym'n condition : T_p=70 °C ; $P_{C_2H_4}$=1.3 bar, P_{H_2}=0.2 bar, Polym'n time=50 min, diluent=toluene.

CONCLUSIONS

In this study, the effect of solvents and pretreatment materials on the impregnation of metallocene and Ziegler-Natta catalysts on a $MgCl_2$ support was investigated. MeOH, EtOH, PrOH, and H_2O were used as solvents, and TiBAL, TMA, and MAO were utilized as pretreatment materials. It was found that recrystallized $MgCl_2$ support exists in the form of $MgCl_2 \cdot n$ (alcohol or H_2O). The amount of solvent remaining in the $MgCl_2$ after recrystallization was closely related to the amount of zirconocene impregnated and its activity. This suggests that the solvent plays an important role in the impregnation of the catalysts. Among the solvents, PrOH resulted in the best condition of the $MgCl_2$ support for zirconocene impregnation. It was shown that an equivalent mole of alkylaluminum should be used to eliminate the residual alcohol or water in the $MgCl_2$ in order to prevent deactivation of the catalyst. TiBAL proved to be the best pretreatment material for alcohol/$MgCl_2$ supports and MAO was superior for $H_2O/MgCl_2$. In the case of CAT1 ($TiCl_4/Cp_2ZrCl_2$/TiBAL/PrOH/$MgCl_2$), the largest amount of Zr was impregnated and the highest molar ratio of Zr/Ti=1/2.71 was attained. CAT2 ($TiCl_4/Cp_2ZrCl_2/MAO/H_2O/MgCl_2$) showed the best hybrid effect for the control of MWD. DSC and GPC results showed that two types of polymer are produced on the hybrid catalysts. The amount of polymer synthesized on the active zirconocene sites decreased in proportion to the amount of TEA. It is concluded that MWD could be controlled on the metallocene/Ziegler-Natta hybrid catalyst supported on the recrystallized $MgCl_2$ by adjusting the amount of MAO and TEA added as a cocatalyst and by the use of different solvents and pretreatment materials.

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