

Synthesis of inorganic MgCl_2 –alcohol adduct via recrystallization method and its application in supported organometallic catalysts for the polymerization of ethylene with 1-hexene

Han Seock Cho, Wha Young Lee*

Division of Chemical Engineering, College of Engineering, Seoul National University, Shinlim-Dong, Kwanak-Ku, Seoul 151-742, South Korea

Received 20 March 2002; accepted 30 April 2002

Dedicated to Professor Wha Young Lee on the occasion of his 65th birthday

Abstract

MgCl_2 –alcohol adduct for use as a catalyst support was prepared by the recrystallization method using alcohol as the dissolution material. The alcohol contents in the support are an important factor in catalysts impregnation. The prepared support was modified by treatment with alkylaluminum compounds. In terms of the treatment of the prepared support, triisobutylaluminum was an excellent pretreatment material. The polymerization of ethylene with 1-hexene was performed over homogeneous and heterogeneous metallocene catalysts. The molecular weight (M_w) and molecular weight distribution (MWD) of copolymers produced by the heterogeneous catalyst were higher and broader than those by homogeneous catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: MgCl_2 –alcohol adduct; Recrystallization; Metallocene catalyst; Ethylene; 1-Hexene; Polymerization

1. Introduction

Metallocene catalyst systems, originally discovered by Sinn and Kaminsky [1], attracted a lot of attention as the next generation of catalysts for olefin polymerization. Olefin copolymers, especially those of ethylene with propylene or another alpha olefin, are of great practical interest. New possibilities for controlling the properties of olefin copolymers via the use of metallocene catalysts have attracted interest from both industry and academy [2,3].

Comonomer insertion into the polymer chain is solely statistical for polymers obtained with metallocene catalysts, as proven by NMR. This phenomenon is contrary to conventional Ziegler–Natta catalysis where the comonomer is mainly incorporated into the low molar mass. Copolymerization with metallocene catalysts extends beyond the capabilities of conventional polymerization catalysts. The copolymerization of ethylene and propylene or 1-butene gives elastomers with different properties [4]. Copolymerization of ethylene with 1,3-butadiene yields polyethylenes which are functionalized by olefinic groups [5]. Along the same line, 4-methyl-1-pentene was copolymerized with ethylene using a chiral and an achiral catalyst [6].

* Corresponding author. Tel.: +82-2-880-7404;
fax: +82-2-888-7295.
E-mail address: wyl@snu.ac.kr (W.Y. Lee).

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 to use the metallocene catalysts in the prevailing slurry or gas phase processes, a procedure for the impregnation of a metallocene catalyst over support is necessary. In addition, since all commercial polymerization processes are used in heterogeneous systems, the preparation of heterogeneous metallocene catalysts is a prerequisite for the existing processes. In recent papers, a variety of supports such as SiO₂, Al₂O₃, zeolite, etc., have been used [7–9].

In this study, based on the above rationale, MgCl₂ was prepared by a recrystallization method using alcohol for the impregnation of metallocene catalysts. The prepared supports and supported metallocene catalysts were characterized by inductively coupled plasma (ICP), thermogravimetric analysis (TGA), gas chromatography (GC), etc. Copolymerization of ethylene with 1-hexene was carried out using Cp₂ZrCl₂ and *rac*-Et[Ind]₂ZrCl₂ catalysts, and especially, the different polymerization behaviors between homogeneous and heterogeneous catalysts were compared. The microstructure of the copolymer was analyzed, and correlated with the physical properties.

2. Experimental

2.1. Materials

High purity N₂ and ethylene (Sinyang gas products) were further purified prior to use by sequentially passing them through columns containing 5 Å molecular sieves (Kokusan Chem.), P₂O₅ (Yakuri Chem.) and RIDOX, an oxygen scavenger (Fischer scientific). The molecular sieves were regenerated at 2-month intervals by treatment with a stream of N₂ at 250 °C and the oxygen scavenger was activated by treatment with a stream of H₂ at 250 °C. Toluene (Oriental Chemical Industry) used as a solvent for the catalyst preparation and polymerization was purified by distillation over elemental sodium to remove residual traces of moisture. 1-Hexene as a comonomer was also purified by reflux over elemental sodium. MgCl₂ (Aldrich Chem.), CH₃OH (Carlo Erba.), C₂H₅OH (Carlo Erba.), *n*-decane (Junsei Chem.), Cp₂ZrCl₂

(Strem Chem.), *rac*-Et[Ind]₂ZrCl₂ (Aldrich Chem.), TIBAL (triisobutylaluminum; Aldrich Chem.), TEA (triethylaluminum; Aldrich Chem.), TMA (trimethylaluminum; Aldrich Chem.), MAO (methylaluminoxane; type 4, Akzo Chem.) were used without further purification.

2.2. Preparation of support and catalyst

MgCl₂ of 0.10 mol (9.52 g) was introduced into a glass reactor equipped with a magnetic stirrer and 100 ml of alcohol was added. The mixture was heated to 60 °C and stirred until the MgCl₂ had completely dissolved. *n*-Decane of 100 ml was then added to this homogeneous solution and the final mixture was stirred at 2000 rpm under vacuum at 80 °C. MgCl₂ particles were slowly precipitated in the *n*-decane medium as the alcohol evaporated. The resulting MgCl₂ particles were washed several times with toluene to remove residual *n*-decane and then dried under vacuum to remove the toluene. Thus, the recrystallized MgCl₂ [MgCl₂·*n*(alcohol)] was obtained [10,11]. Support of 5 g was introduced into a 500 ml flask equipped with a water-cooled reflux condenser and a magnetic stirrer. Toluene of 100 ml was added and the alkylaluminum compounds was then added to the flask. The mixture was stirred at 0, 20, 40, 60 °C for 30 min, respectively, and then stirred at 80 °C for 2 h. The mixture was then washed with toluene to remove the unreacted alkylaluminum and finally dried under vacuum to give the alkylaluminum/MgCl₂·*n*(alcohol). Washed supports of 2 g were suspended in 100 ml of toluene and reacted with 0.10 g of Cp₂ZrCl₂ or *rac*-Et[Ind]₂ZrCl₂ at 50 °C for 2 h and then washed in the same manner (denoted as Cp₂ZrCl₂ or *rac*-Et[Ind]₂ZrCl₂/alkylaluminum/MgCl₂·*n*(alcohol)).

2.3. Characterization

To determine the alcohol contents in the recrystallized MgCl₂, gas chromatography (GC; Yanaco G1700, Porapak Q column) and thermogravimetric analysis (TGA; Perkin-Elmer, TGA7) were used. The temperature at which alcohol desorbed was examined by differentiating TGA thermogram. The titanium and zirconium contents of the catalysts were measured using inductively coupled plasma (ICP; VG PQ2-Turbo, VG elemental). The interaction behavior

between the catalyst and alkylaluminum compounds was investigated by ^{27}Al -NMR (^{27}Al -NMR; Varian, 200 MHz Oxford Co.). The differential scanning calorimetry (DSC; Dupont V4.0B) was carried out under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The molecular weight (Mw) and molecular weight distribution (MWD) were measured by gel permeation chromatography (GPC; PL-210, Polymer Laboratory) at 160°C with 1,2,4-trichlorobenzene as the solvent. The microstructure and 1-hexene contents in the copolymer were measured by ^{13}C -NMR (Varian unity Plus 300).

2.4. Polymerization of ethylene and ethylene/1-hexene

Toluene of 300 ml and cocatalyst were introduced into a 1 l glass reactor under a stream of N_2 and then evacuated to remove N_2 . Ethylene was then fed at a constant pressure of 1.5 bar. In the copolymerization, ethylene was continuously supplied to a toluene solution containing 1-hexene. 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 a dilute hydrochloric acid solution in methanol and the polymer was isolated and dried. The polymerization rate was determined from the amount of consumed ethylene, measured using a mass flow meter.

3. Results and discussion

3.1. 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 $2\theta = 15^\circ$ (003 plane), 35° (004 plane) and 50° (110 plane) [12]. 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 $\text{MgCl}_2 \cdot n\text{CH}_3\text{OH}$ was formed during the preparation of the MgCl_2 by the recrystallization method. The approximate value of n is 4, based on the calculated

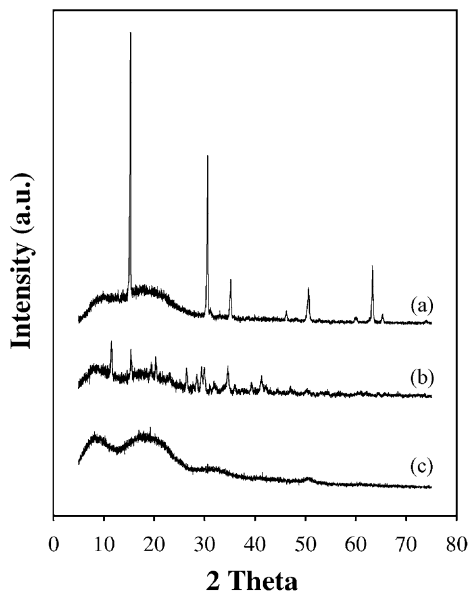


Fig. 1. XRD patterns of the recrystallized MgCl_2 : (a) anhydrous MgCl_2 ; (b) $\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$; (c) TIBAL/ $\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$.

methanol content as shown in Table 1. Fig. 2(a) shows the proposed structure of the $\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$. In addition, the support structure was varied with respect to the dissolution material. When MgCl_2 was recrystallized using ethanol as a solvent, the structure was $\text{MgCl}_2 \cdot 3.33\text{C}_2\text{H}_5\text{OH}$ as shown in Fig. 2(b).

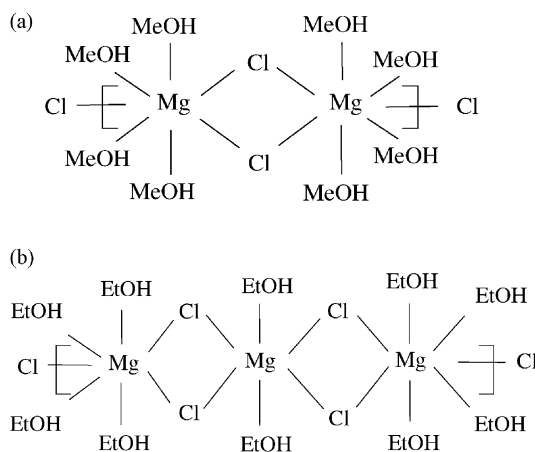


Fig. 2. The proposed structure of the recrystallized MgCl_2 : (a) $\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$; (b) $\text{MgCl}_2 \cdot 3.33\text{C}_2\text{H}_5\text{OH}$.

Table 1
Characteristics of MgCl₂ prepared by the recrystallization method and various catalysts

Supports and catalysts	Alcohol content (wt.%)	Surface area (m ² /g)	Pretreatment concentration (mol/l)	Zr (wt.%)
Anhydrous MgCl ₂	–	1.7	–	–
MgCl ₂ ·4CH ₃ OH	56.5	14.1	–	–
MgCl ₂ ·3.33C ₂ H ₅ OH	61.3	12.3	–	–
MgCl ₂ ·4CH ₃ OH at 100 °C	13.4	16.8	–	–
MgCl ₂ ·4CH ₃ OH at 200 °C	7.21	20.5	–	–
Cp ₂ ZrCl ₂ /TMA/MgCl ₂ ·4CH ₃ OH	–	n.d.	0.6	0.056
Cp ₂ ZrCl ₂ /TEA/MgCl ₂ ·4CH ₃ OH	–	n.d.	0.6	0.44
Cp ₂ ZrCl ₂ /MAO/MgCl ₂ ·4CH ₃ OH	–	n.d.	0.6	0.14
Cp ₂ ZrCl ₂ /MgCl ₂ ·4CH ₃ OH	54.3	14.3	–	–
Cp ₂ ZrCl ₂ /TIBAL/MgCl ₂ ·4CH ₃ OH at 100 °C	–	42.3	0.3	0.012
Cp ₂ ZrCl ₂ /TIBAL/MgCl ₂ ·4CH ₃ OH at 200 °C	–	39.8	0.2	–
Cp ₂ ZrCl ₂ /TIBAL/MgCl ₂ ·4CH ₃ OH	–	382.1	0.6	1.02
	–	209.4	0.3	0.43
	–	68.3	0.15	–
Et[Ind] ₂ ZrCl ₂ /TIBAL/MgCl ₂ ·3.33C ₂ H ₅ OH	–	412.1	0.6	0.69

To examine the desorption temperature of methanol, the support was scanned from 30 to 300 °C by TGA under a N₂ 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-thermally treated MgCl₂·4CH₃OH desorbed at around 110, 140 and 250 °C, respectively,

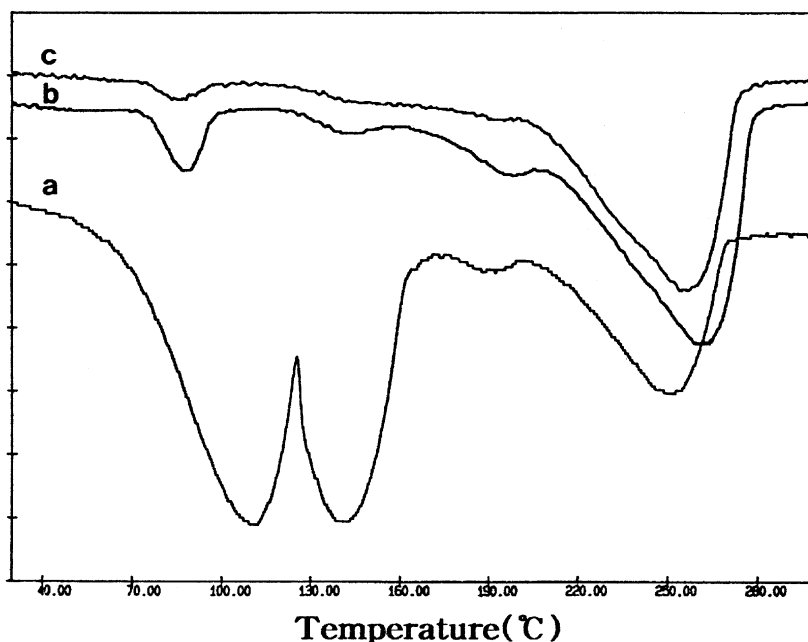


Fig. 3. DTGA thermograms of supports: (a) recrystallized MgCl₂·4CH₃OH; (b) MgCl₂·4CH₃OH at 100 °C; (c) MgCl₂·4CH₃OH at 200 °C. Thermally pretreated at 100 or 200 °C for 2 h under N₂ atmosphere.

thus giving the methoxy groups in the support as shown in Eq. (1) [13] as follows:

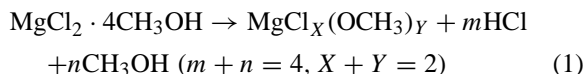


Table 1 shows that the methanol contents in the thermally treated supports decrease drastically with increasing treatment temperature, suggesting that considerable amounts of methoxy groups exist in the support after thermal pretreatment.

3.2. 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 [14]. 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 [15]. 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 1, 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 1 show that the impregnated content of Cp_2ZrCl_2 increased with increasing levels of TIBAL pretreatment, and that the surface area of the catalyst 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 due to the fact that 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, aluminum methoxides formed by the reaction between methanol and alkylaluminum create the impregnation sites for Cp_2ZrCl_2 . The proposed impregnation mechanism of the metallocene catalysts is shown in Fig. 4.

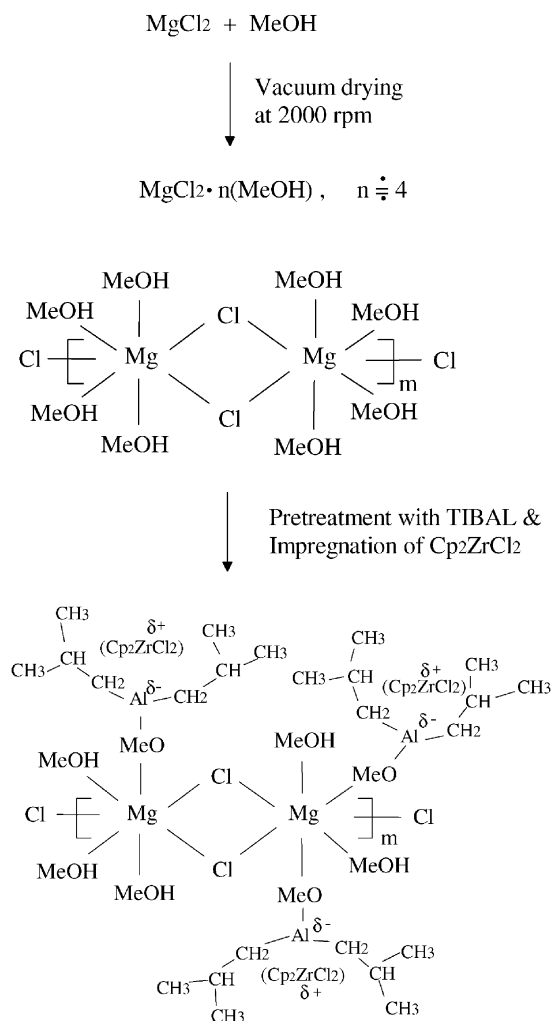


Fig. 4. Proposed mechanism for the impregnation of the metallocene catalysts over the recrystallized MgCl_2 .

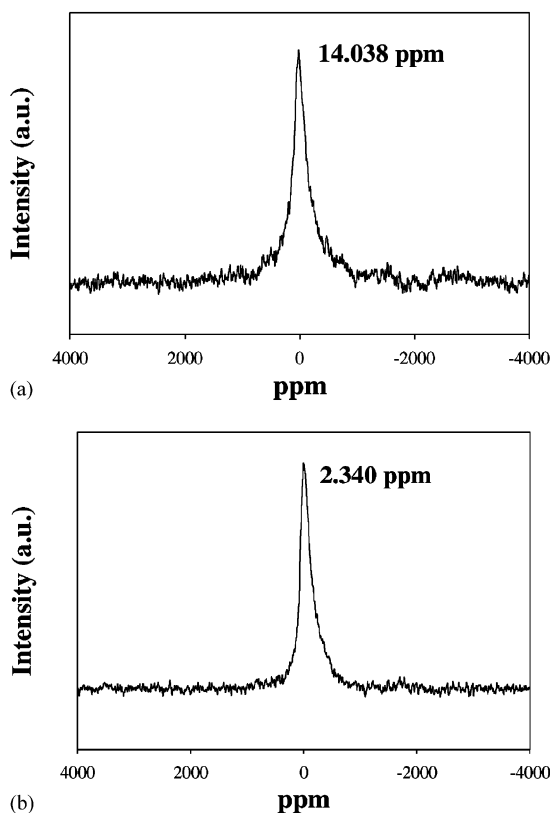


Fig. 5. ²⁷Al-NMR peaks of support and catalyst: (a) TIBAL/MgCl₂·4CH₃OH; (b) Cp₂ZrCl₂/TIBAL/MgCl₂·4CH₃OH.

3.3. Interaction behavior between catalyst and alkylaluminum compounds

Fig. 5 shows the ²⁷Al-NMR spectra of TIBAL-treated support and supported metallocene catalyst. The Al peak in the TIBAL-treated support appeared at 14.038 ppm, while that of the supported metallocene catalyst appeared at 2.340 ppm. The higher electron density of Cp₂ZrCl₂ shielded that of Al in the TIBAL-treated support, and therefore, the Al peak appeared in the region of upfield shifting from 14.038 to 2.340 ppm. This suggests that the strong interaction between the TIBAL and the metallocene catalyst exists, and TIBAL plays a role for the impregnation of the catalysts.

To examine the catalytic behavior with respect to temperature, the detection temperature was varied from 25 to 70 °C. With increasing the temperature,

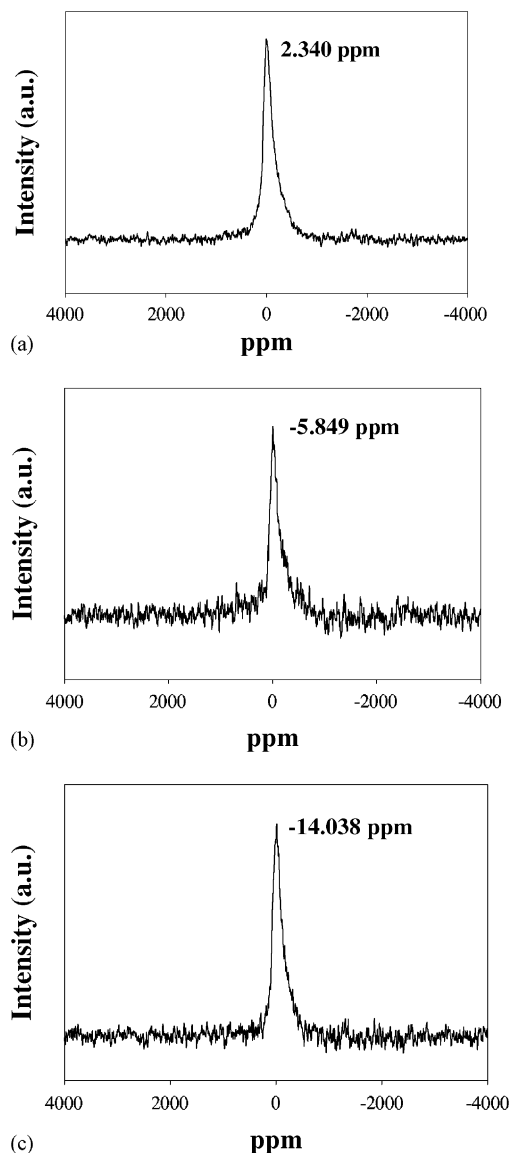


Fig. 6. ²⁷Al-NMR peaks of the Cp₂ZrCl₂/TIBAL/MgCl₂·4CH₃OH with respect to temperatures: (a) 25, (b) 50 and (c) 70 °C.

Al peak drastically shifts from downfield to upfield, as shown in Fig. 6. The reason why the Al peak shifts to the downfield is attributed to the fact that the molecular movements of the catalyst is more active at the higher temperature, and therefore, the interaction between catalyst and common alkylaluminums is weakened.

Table 2

Analytical data of the ethylene/1-hexene copolymer catalyzed over Cp_2ZrCl_2 and $\text{Cp}_2\text{ZrCl}_2/\text{TIBAL}/\text{MgCl}_2\cdot 4\text{CH}_3\text{OH}^{\text{a}}$

Catalyst	1-Hexene concentration (mol/l)	Activity ^b	T_m (°C)	Crystallinity, X_c (%)	1-Hexene content (mol%)	Mw ($\times 10^{-4}$)	MWD
$\text{Cp}_2\text{ZrCl}_2^{\text{c}}$	–	28.8	134.2	66.5	–	10.6	2.14
	0.1	63.3	120.2	54.0	1.51	4.48	2.23
	0.3	56.6	112.3	42.4	3.19	2.88	2.72
	0.5	46.7	105.5	37.0	4.06	2.32	2.81
	1.0	19.2	89.7	14.8	8.29	1.50	2.60
$\text{Cp}_2\text{ZrCl}_2/\text{TIBAL}/\text{MgCl}_2\cdot 4\text{CH}_3\text{OH}^{\text{d}}$	–	7.5	134.5	64.0	–	44.0	3.51
	0.1	18.7	130.3	62.1	0.40	24.3	3.38
	0.3	11.7	128.5	59.2	0.54	19.3	3.66
	0.5	10.4	126.2	53.7	0.70	13.9	3.35
	1.0	5.9	124.8	40.0	0.86	7.85	3.67

^a Conditions: $T_p = 50^\circ\text{C}$, $P_{\text{C}_2\text{H}_4} = 1.5$ atm, polymerization time = 20 min, solution (toluene + 1-hexene) = 300 cm^3 .^b Activity: kg polymer/g [Zr].^c Catalyst = 3.12×10^{-4} g [Zr], MAO = 0.14 mol/l.^d Catalyst = 4.5771×10^{-4} g [Zr], MAO = 0.083 mol/l.

3.4. Characteristics of ethylene/1-hexene copolymerization over homogeneous and heterogeneous metallocene catalysts

In order to observe the effect of comonomer concentration on activity, copolymerization of ethylene with 1-hexene was performed in the wide range of comonomer concentration. As shown in Tables 2 and 3, in all range of mole fraction of comonomer except 1.0 M concentration, activity was enhanced by an addition of comonomer. This effect is mainly due to the increase of propagation rate constant, K_p , as discussed by many researchers [16]. On the other

hand, it has been found that too excess of comonomer drastically lowers the activity in both homogeneous and heterogeneous catalysts, suggesting that the insertion of ethylene was interrupted. This results show that there is an optimum condition for the copolymerization and that an obvious difference of kinetic behavior exists for copolymerization under high mole percent of 1-hexene in monomer feed.

Comparing the activities of homogeneous catalyst (Cp_2ZrCl_2) with those of heterogeneous catalyst ($\text{Cp}_2\text{ZrCl}_2/\text{TIBAL}/\text{MgCl}_2\cdot 4\text{CH}_3\text{OH}$) in Table 2, the activity of the heterogeneous catalyst was about several times lower under the same condition because

Table 3

Analytical data of the ethylene/1-hexene copolymer catalyzed over $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2/\text{TIBAL}/\text{MgCl}_2\cdot 3.33\text{C}_2\text{H}_5\text{OH}^{\text{a}}$

Catalyst	1-Hexene concentration (mol/l)	Activity ^b	T_m (°C)	Crystallinity, X_c (%)	1-Hexene content (mol%)	Mw ($\times 10^{-4}$)	MWD
$\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2/\text{TIBAL}/\text{MgCl}_2\cdot 3.33\text{C}_2\text{H}_5\text{OH}^{\text{c}}$	–	2.61	132.3	63.0	–	36.7	3.78
	0.1	7.29	112.0	43.6	3.78	22.0	3.59
	0.3	5.32	88.7	27.6	8.31	12.1	3.44
	0.5	4.11	82.1	16.3	13.4	11.4	3.05
	1.0	1.77	n.d.	n.d.	17.7	7.48	2.89

^a Conditions: $T_p = 50^\circ\text{C}$, $P_{\text{C}_2\text{H}_4} = 1.5$ atm, polymerization time = 20 min, solution (toluene + 1-hexene) = 300 cm^3 .^b Activity: kg polymer/g [Zr].^c Catalyst = 4.554×10^{-4} g [Zr], MAO = 0.083 mol/l.

Table 4
Chain sequence distribution of ethylene/1-hexene copolymer catalyzed over Cp_2ZrCl_2 and $\text{Cp}_2\text{ZrCl}_2/\text{TIBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}^a$

Catalyst	1-Hexene concentration (mol/l)	EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH	r_E	r_H
Cp_2ZrCl_2	0.1	0.9593	0.0263	0.0046	0.0098	–	–	0.9725	0.0275	–	70.7	–
	0.3	0.9154	0.0489	0.0110	0.0247	–	–	0.9399	0.0601	–	31.3	–
	0.5	0.8863	0.0692	0.0081	0.0364	–	–	0.9209	0.0791	–	23.3	–
	1.0	0.8014	0.0962	0.0501	0.0523	–	–	0.8415	0.1505	–	11.2	–
$\text{Cp}_2\text{ZrCl}_2/\text{TIBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$	0.1	0.9891	0.0078	0.0011	0.0020	–	–	0.9930	0.0070	–	283.7	–
	0.3	0.9856	0.0092	0.0019	0.0033	–	–	0.9902	0.0098	–	202.1	–
	0.5	0.9810	0.0106	0.0021	0.0063	–	–	0.9863	0.0137	–	144.0	–
	1.0	0.9760	0.0151	0.0019	0.0070	–	–	0.9834	0.0166	–	118.5	–

^a Conditions: $T_p = 50^\circ\text{C}$, $P_{\text{C}_2\text{H}_4} = 1.5 \text{ atm}$, polymerization time = 20 min, solution (toluene + 1-hexene) = 300 cm^3 .

Table 5
Chain sequence distribution of ethylene/1-hexene copolymer catalyzed over *rac*-Et[Ind]₂ZrCl₂/TIBAL/MgCl₂·3.33C₂H₅OH^a

Catalyst	1-Hexene concentration (mol/l)	EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH	<i>r</i> _E	<i>r</i> _H
<i>rac</i> -Et[Ind] ₂ ZrCl ₂ /TIBAL/MgCl ₂ ·3.33C ₂ H ₅ OH	0.1	0.8868	0.1013	0.0010	0.0109	–	–	0.9375	0.0625	–	30.0	–
	0.3	0.7974	0.1081	0.0378	0.0479	0.0088	–	0.8515	0.1441	0.0044	11.8	0.0611
	0.5	0.6760	0.1696	0.0517	0.0769	0.0258	–	0.7608	0.2263	0.0129	6.72	0.114
	1.0	0.5918	0.1723	0.0797	0.1139	0.0423	–	0.6780	0.3008	0.0212	4.51	0.141

^a Conditions: *T*_p = 50 °C, *P*_{C₂H₄} = 1.5 atm, polymerization time = 20 min, solution (toluene + 1-hexene) = 300 cm³.

one side of the metallocene catalyst is blocked by the support. On the other hand, the melting temperature (T_m) of the copolymer produced by the heterogeneous catalyst was higher than that by the homogeneous catalyst due to the interruption of the insertion of 1-hexene over heterogeneous catalyst.

In Tables 2 and 3, the Mw increased and the MWD broadened for the copolymers produced by the heterogeneous metallocene catalysts. In this case, the necessary bimolecular reaction between two metallocene active sites, that makes the β -hydrogen transfer possible, is hindered due to the immobilization of the catalysts over the support, resulting in a longer polymer chain, i.e., higher Mw. In addition, when the metallocene catalyst is impregnated over the support, a large portion of the metallocene catalyst is destroyed by acid centers. As a result, the MWD of the polymer produced by the heterogeneous catalysts is more broader than that by the homogeneous catalysts [17]. The polymerization behavior and the properties of the copolymer over the ansa metallocene catalysts are considerably different from those of the unbridged metallocenes. The results in Table 3 show that the insertion of 1-hexene over *rac*-Et[Ind]₂ZrCl₂ is more effective than that of Cp₂ZrCl₂ as shown in Table 2. This different copolymerization behavior can be induced from the catalyst molecular structure. For C₂ symmetric ansa bridged catalyst, *rac*-Et[Ind]₂ZrCl₂, the angle between two ligands is about 62° and the Cl–Zr–Cl angle is about 99°. On the other hand, for C_{2v} unbridged catalyst, Cp₂ZrCl₂, the angle between two ligands is about 53°, and the Cl–Zr–Cl angle is about 94°. Since the angle between two ligands is large in bridged ansa metallocenes, the active site of metallocene catalyst is exposed out to interact with MAO and comonomer insertion, resulting in the copolymer containing much 1-hexene content.

3.5. The microstructure of copolymer

As shown in Tables 4 and 5, the triad distributions of ethylene/1-hexene copolymer can be determined from the ¹³C-NMR spectra following the assignment method according to Randall [18]. Conditional probability of chain end unit can be calculated according to the following equations, where P(A/B) is a probability that an A event occurs given that B event has

previously occurred.

$$P\left(\frac{E}{E}\right) = \frac{[EE]}{[E]}, \quad P\left(\frac{H}{E}\right) = \frac{[EH]}{2[E]},$$

$$P\left(\frac{E}{H}\right) = \frac{[EH]}{2[H]}, \quad P\left(\frac{H}{H}\right) = \frac{[HH]}{[H]}$$

The copolymerization parameter, r_E , which describes how much faster an ethylene unit is incorporated into the growing polymer chain than 1-hexene, if the last inserted monomer was an ethylene unit. The copolymerization parameter, r_H , is the analogous ratio for the 1-hexene. Reactivity ratio of ethylene (r_E) and of 1-hexene (r_H) can be calculated as following equations from the calculated probability, where X is the monomer ratio, [E]/[H] in feed.

$$r_E = \frac{P(E/E)}{X} P\left(\frac{H}{E}\right) = \frac{2[EE]}{[EH + HE]},$$

$$r_H = X \frac{P(H/H)}{P(E/H)} = \frac{2[HH]}{[EH + HE]}$$

In Table 4, r_E values of copolymer produced by the homogeneous catalyst are smaller than those of heterogeneous catalyst. This result indicates that the insertion of the 1-hexene into the growing polymer chain is more effective over homogeneous catalyst than that of the heterogeneous catalyst. This effect is more clear with the increase of the 1-hexene concentration. For Cp₂ZrCl₂ catalyst, the triad of [HHE + EHH] and [HHH] could not be detected, indicating that the probability of the 1-hexene insertion after the 1-hexene monomer is too difficult to incorporate.

However, the *rac*-Et[Ind]₂ZrCl₂ supported catalysts could polymerize ethylene with 1-hexene well, indicating the [HHE + EHH] triad signals in Table 5. As previously mentioned, the active site of ansa metallocene catalyst is exposed to interact with comonomer, and therefore, the 1-hexene easily contact the active sites.

4. Conclusions

MgCl₂-alcohol adduct for use as a catalyst support was prepared by the recrystallization method using alcohol as the dissolution material. The alcohol contents in the support affect the impregnation of

metallocene catalysts. In terms of the treatment of the prepared support, TIBAL was an excellent pretreatment material.

The copolymerization of ethylene with 1-hexene was performed over homogeneous and heterogeneous metallocene catalysts. At a wide range of comonomer concentration, comonomer effect, i.e., the activity enhancement by an addition of comonomer was observed. However, too excess of comonomer contents lowers the activity, suggesting that there is an optimum condition for the copolymerization of ethylene and 1-hexene. For the copolymers produced by the heterogeneous catalyst, M_w increased due to the immobilization of the catalysts which interrupt the bimolecular reaction, and MWD was broadened resulting from the different active sites.

Microstructure in the copolymer indicates that the supported *rac*-Et[Ind]₂ZrCl₂ catalysts could polymerize ethylene with 1-hexene well, suggesting the active site of ansa metallocene catalyst is exposed to interact with comonomer, and therefore, the 1-hexene easily contacts the active sites.

Acknowledgements

This paper is dedicated to Prof. Wha Young Lee in memory of his 65th birthday. The authors acknowledge the research fund from the LG Chemical.

References

- [1] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* 18 (1980) 99.
- [2] N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356.
- [3] A. Zambelli, C. Pellecchia, L. Oliva, P. Longo, A. Grassi, *Makromol. Chem.* 192 (1991) 223.
- [4] V. Banzi, L. Angiolini, D. Caretti, C. Carlini, *Angew. Makromol. Chem.* 229 (1995) 113.
- [5] W. Kaminsky, M. Schlobohm, *Makromol. Chem., Macromol. Symp.* 4 (1986) 103.
- [6] W. Kaminsky, *Angew. Makromol. Chem.* 145 (1986) 149.
- [7] K. Soga, M. Kaminaka, *Macromol. Chem., Rapid Commun.* 13 (1992) 221.
- [8] H.S. Cho, D.J. Choi, W.Y. Lee, *J. Appl. Polym. Sci.* 78 (2000) 2318.
- [9] S.I. Woo, Y.S. Ko, T.K. Han, J.W. Park, W.S. Huh, in: *Proceeding of the Metallocenes'96*, Schotland Business Research, Germany, 1986, p. 271.
- [10] H.M. Park, W.Y. Lee, *Eur. Polym. J.* 28 (1992) 1417.
- [11] H.S. Cho, J.S. Chung, W.Y. Lee, *J. Mol. Catal. A* 159 (2000) 203.
- [12] D.N.T. Magalhaes, O.D.C. Filho, F.M.B. Coutinho, *Eur. Polym. J.* 27 (1991) 827.
- [13] D.N.T. Magalhaes, O.D.C. Filho, F.M.B. Coutinho, *Eur. Polym. J.* 27 (1991) 1093.
- [14] K. Soga, M. Kaminaka, *Macromol. Chem., Rapid Commun.* 13 (1992) 221.
- [15] K. Soga, M. Kaminaka, *Makromol. Chem., Rapid Commun.* 12 (1991) 367.
- [16] J. Koivumaki, J.V. Seppala, *Macromolecules* 26 (1993) 5535.
- [17] W. Kaminsky, *Macromol. Chem. Phys.* 197 (1996) 3907.
- [18] J.C. Randall, *JMS-Rev. Macromol. Chem. Phys. C* 29 (2–3) (1989) 201.