

Control of molecular weight distribution for polyethylene catalyzed over Ziegler–Natta/Metallocene hybrid and mixed catalysts

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Abstract

Two types of inorganic supports, MgCl_2 and SiO_2 , for use in the impregnation of catalysts, were prepared by the recrystallization and the sol–gel methods, respectively. The Ziegler–Natta/Metallocene hybrid and mixed catalysts were prepared in order to control the molecular weight (Mw) and the molecular weight distribution (MWD) during ethylene polymerization. The polyethylene produced by the Ziegler–Natta/Metallocene hybrid and mixed catalysts showed two melting temperatures and a bimodal MWD, corresponding to products arising from each of the individual catalysts. This suggests that these Ziegler–Natta/Metallocene catalysts acted as individual active species and produced a blend of polymers. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metallocene catalyst; Ziegler–Natta catalyst; Ziegler–Natta/Metallocene hybrid catalysts; Ziegler–Natta/Metallocene mixed catalysts; Ethylene polymerization

1. Introduction

In polymer processing, the molecular weight (Mw) and the molecular weight distribution (MWD) represent basic properties, which serve as determinants of polymer properties. It is generally accepted that the Mw is a major determinant of mechanical properties, while MWD is largely responsible for rheological properties. Although high-Mw polyethylene has superior

physical properties, it is difficult to process. On the other hand, an increase in MWD tends to improve flowability at high shear rates, which is an important factor in blowing and extrusion techniques [1,2]. Therefore, it is necessary to control the Mw, as well as the MWD of polymers in order to optimize both mechanical and rheological properties.

Several methods for controlling the Mw and the MWD of polymers are available. The first involves physically blending the polymers with different average Mw. Although blends can be used to control the Mw and the MWD of polymers, they contain high gel levels, and as a

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result, miscibility problems can arise. The second method involves the use of a series of reactors, each of which supports polymerization under different conditions such as temperature, pressure, and hydrogen partial pressure, etc. However, this method is not acceptable because it involves additional processes and increases capital cost considerably. The third method is to combine two or more transition metal catalysts in a single reactor, thus producing polymers with different Mw ranges [3]. In this case, a highly advanced catalyst technology is required.

Studies in this area to date have dealt with the use of catalyst mixtures that are homogeneous [4,5]. However, a limited number of reports have been published, which deal with MWD in heterogeneous types of catalysts. From the practical viewpoint of polymer processes, in order for catalysts to be used in the prevailing slurry or gas phase processes, it is necessary to modify them to a supported form. In this study, which is based on the above rationale, supported Ziegler–Natta/Metallocene hybrid catalysts and combinations of metallocene supported and Ziegler–Natta supported catalysts were used to control the MWD of polyethylene. In addition, two types of new inorganic supports, recrystallized magnesium dichloride and silica, were prepared for use as impregnation catalysts. A magnesium dichloride support was prepared by the recrystallization method using methanol as a solvent and the silica support was developed by means of a sol–gel method. These two types of supports were useful for the impregnation of catalysts and ethylene polymerization was performed with the Ziegler–Natta/Metallocene hybrid and mixed catalysts, which had been impregnated on these supports.

2. Experimental

2.1. Materials

High-purity ethylene and N₂ (Sinyang Gas Products) were purified by sequential passage

through columns containing 5 Å molecular sieves (Kokusan), and anhydrous P₂O₅ (Yakuri). Toluene (Oriental) was purified by distillation over sodium metal. MgCl₂ (Aldrich), CH₃OH (Carlo Erba), *n*-decane (Aldrich), colloidal SiO₂ (LUDOX HS-40, Dupont), Cp₂ZrCl₂ (Strem), TiCl₄ (Aldrich), triisobutylaluminum (TiBAL; Aldrich), triethylaluminum (TEA; Aldrich), and methylaluminoxane (MAO; type 4, Akzo) were used without further purification.

2.2. Preparation of supports and catalysts

2.2.1. Preparation of MgCl₂ by the recrystallization method and catalyst impregnation

Anhydrous MgCl₂, 0.10 mol, was introduced into a glass reactor equipped with a magnetic stirrer and 2.47 mol of methanol was then added. The mixture was heated to 60°C and stirred until the MgCl₂ had completely dissolved. *n*-Decane, 0.51 mol, was then added to this solution and the mixture was stirred at 2000 rpm under vacuum at 80°C. MgCl₂ particles slowly precipitated in the *n*-decane medium as the methanol evaporated. The resulting MgCl₂ particles were washed with toluene to remove the residual *n*-decane and then dried under vacuum to remove the toluene, to give recrystallized MgCl₂ (MgCl₂ · 4CH₃OH).

Recrystallized MgCl₂, 22.4 mmol, was introduced into a 500-ml flask equipped with a water-cooled reflux condenser and a magnetic stirrer. TiBAL was then added to the flask, based on the methanol content in the support and 0.94 mol of toluene was added. The mixture was stirred at 0°C, 20°C, 40°C, and 60°C for 30 min, respectively, and then stirred at 80°C for an additional 2 h. The mixture was then washed to remove the unreacted TiBAL and finally dried under vacuum to give the TiBAL/MgCl₂ · 4CH₃OH. TiBAL-treated recrystallized MgCl₂, 8.95 mmol, was suspended in 0.94 mol of toluene and reacted with 1.03 mmol of Cp₂ZrCl₂ at 50°C for 2 h and then washed in

the same manner. TiCl_4 , 18.2 mmol, was introduced into this catalyst, and the mixture was stirred for 2 h at 70°C. After the reaction, the mixture was washed with toluene to give the final Ziegler–Natta/Metallocene hybrid catalysts. These hybrid catalysts, denoted as $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, were suspended in 0.94 mol of toluene and used directly as catalysts. TiBAL-treated recrystallized MgCl_2 , 8.95 mmol, was reacted with 45.5 mmol of TiCl_4 at 70°C for 2 h and then washed to give $\text{TiCl}_4/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$.

2.2.2. Preparation of SiO_2 by the sol–gel method and catalyst impregnation

MgCl_2 was dissolved in 5.55 mol of distilled water. The solution was introduced into a 4-l reactor which contained 2.5 l of corn oil and was stirred at 2000 rpm in order to uniformly disperse the solution in the oil. Colloidal SiO_2 , 1.73 mol, was then introduced to this slurry to initiate gelation between the stable silica sol and Mg^{+2} . The particles were separated, washed with toluene, and dried at 80°C for 24 h (SiO_2). Toluene, 0.94 mol, was introduced into a glass reactor, after which 83.2 mmol of support was suspended in it. One hundred millimoles of MAO was added at 0°C, and the mixture was stirred at 0°C, 20°C, 40°C, and 60°C for 30 minutes and then stirred at 80°C for an additional 2 h. This mixture was then washed and dried under vacuum (MAO/SiO_2).

MAO-treated silica support, 33.3 mmol, was suspended in 0.94 mol of toluene and reacted with 1.03 mmol Cp_2ZrCl_2 at 50°C for 2 h and then washed ($\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$). TiCl_4 , 18.2 mmol, was introduced into this slurry. The mixture was then stirred at 70°C for 2 h, and washed to give $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$. MAO-treated support, 33.3 mmol, was reacted with 45.5 mmol of TiCl_4 at 70°C for 2 h and then washed to give $\text{TiCl}_4/\text{MAO}/\text{SiO}_2$.

2.3. Characterization

The elemental contents of aluminum, zirconium and titanium in the catalyst were

determined by ICP (VG PQ2-Turbo from VG elemental). The methanol content of the recrystallized MgCl_2 samples was determined by TGA (Perkin-Elmer TGA7). XRF (Shimadzu-1700) was used to determine the Mg and Si content of the support. The relative elemental surface ratios of Si:Mg:Cl on the support were measured by SEM-EDS (JSM-840 A, JEOL). The surface area of the catalysts was determined with an N_2 -BET analyzer (ASAP-2000, Micromeritics). An analysis by DSC (V 4.0B from Dupont) was carried out and recorded for the first run under a nitrogen atmosphere at a heating rate of 10°C/min. The Mw and MWD of polyethylene were determined by GPC (PL-210, Polymer Laboratory) at 160°C with 1,2,4-trichlorobenzene as a solvent. The polyethylene was separated from the support by filtering the support in the molten state.

2.4. Polymerization of ethylene

2.8 mol of toluene and cocatalyst were introduced into a 1-l glass reactor equipped with a magnetic stirrer under a stream of N_2 and the reactor was then evacuated to remove the N_2 . Hydrogen was fed into the reactor prior to the introduction of ethylene, and ethylene was then fed into the reactor at a constant pressure. The polymerization reaction was initiated by introducing the catalyst suspension into the reactor with a syringe. The polymerization reaction was terminated after 50 min by adding an excess of dilute hydrochloric acid solution in methanol, and the resulting polymer was isolated and dried. The polymerization rate was determined from the amount of consumed ethylene, which was measured with a mass flowmeter.

3. Results and discussion

3.1. Characteristics of MgCl_2 prepared by the recrystallization method and impregnation of catalysts

Anhydrous MgCl_2 has a cubic close packing structure, which gives a strong XRD pattern at

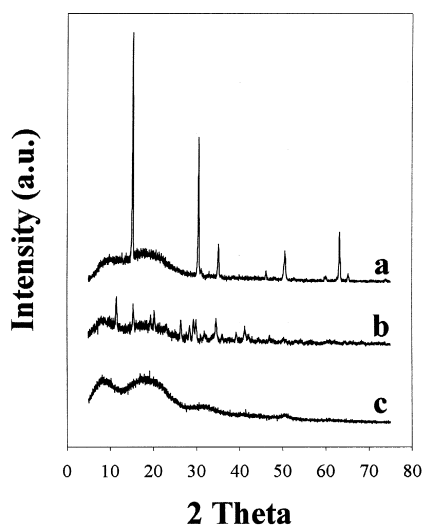


Fig. 1. XRD patterns of the recrystallized MgCl_2 : (a) anhydrous MgCl_2 ; (b) $\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$; (c) $\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$.

$2\theta = 15^\circ$ (003 plane), 35° (004 plane) and 50° (110 plane) [6]. 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, and that the ap-

proximate value of n is 4, based on the calculated methanol content.

It is well known that if metallocene is directly impregnated on supports without any modification of their surfaces, the catalytic activity and the degree of impregnation are typically low [7]. 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 [8]. In this study, the surface condition of the recrystallized MgCl_2 was modified by treatment with TiBAL.

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. Such aluminum methoxides, which are formed via the reaction of methanol in the support with TiBAL, are important because these chemical complexes create impregnation sites for the metallocene catalysts.

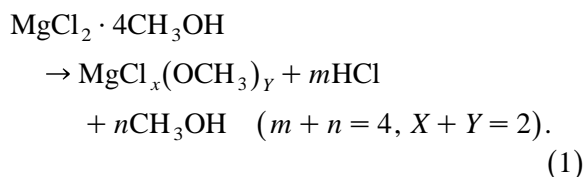
The results in Table 1 show that the impregnation contents of Cp_2ZrCl_2 increased with increasing levels of TiBAL pretreatment, and that the surface area of the catalyst drastically in-

Table 1

Characteristics of MgCl_2 prepared by the recrystallization method and various catalysts

Supports and catalysts	Alcohol content (mmol)	Surface area (m^2/g)	TiBAL pretreatment concentration (mol/l)	Zr (mmol)	Ti (mmol)
anhydrous MgCl_2	–	1.7	–	–	–
$\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$	17.6	14.1	–	–	–
$\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH} - 100^\circ\text{C}$	4.18	16.8	–	–	–
$\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH} - 200^\circ\text{C}$	2.25	20.5	–	–	–
$\text{Cp}_2\text{ZrCl}_2/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$	16.9	14.3	–	–	–
$\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH} - 100^\circ\text{C}$	–	42.3	0.3	0.00132	–
$\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH} - 200^\circ\text{C}$	–	39.8	0.2	–	–
$\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$	–	382.1	0.6	0.112	–
		209.4	0.3	0.0471	–
		68.3	0.15	–	–
$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$	–	428.5	0.6	0.0954	0.516
$\text{TiCl}_4/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$	–	412.7	0.6	–	0.601

creased 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°C and 200°C, respectively, followed by the reaction with TiBAL, based on the residual methanol content. 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) [9].



Consequently, it is noteworthy that the modification of recrystallized MgCl_2 by pretreatment with TiBAL provides for the impregnation of the metallocene catalyst. This result is important because the majority of inorganic supports impregnate only small amounts of catalyst [10].

3.2. Characteristics of SiO_2 prepared by the sol–gel method and impregnation of catalysts

Fig. 2 shows a proposed mechanism for the formation of the silica support. Particles of the colloidal sol are approximately 12 nm in diameter. These particles contain negative charges on their surfaces, which serve to suppress the gelation of particles [11]. When a MgCl_2 solution is added to this stable sol, the dissolved magnesium salt neutralizes the negative charge on the surface of the stable sol, and as a result, the silica sol undergoes gelation via dimerization, trimerization and further polymerization. Table 2 shows the characteristics of the silica support. The difference in the relative mole ratio of Mg/Si between in the bulk and on the surface of the support was from 30 to 65 (mol/mol), suggesting that magnesium is reasonably well distributed throughout the interior and exterior portions of the supports. In addition, the relative mole ratio of $\text{Si}:\text{Mg}:\text{Cl}$ on the surface of the

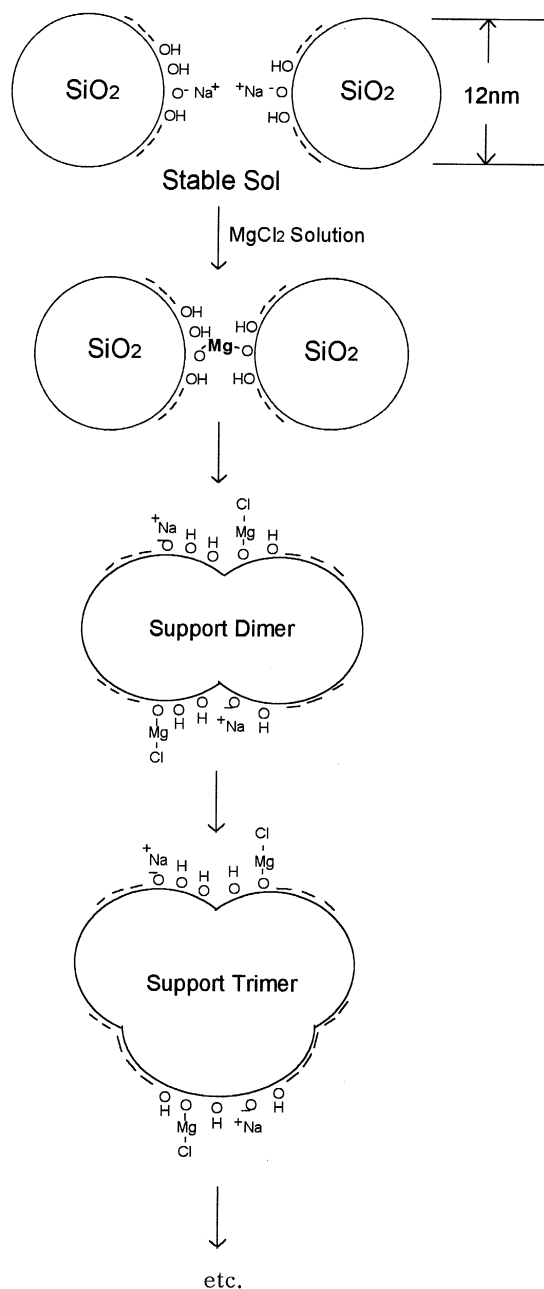


Fig. 2. Proposed mechanism of the reaction between colloidal SiO_2 and MgCl_2 solution.

support indicates that hydroxyl groups on the surface of colloidal silica interact with Mg^{+2} during the formation of the support, thus generating magnesium oxide complexes ($-\text{Si}-\text{O}-$

Mg–Cl). As shown in Table 2, the Mg contents affect the surface area and the impregnation contents of catalysts. Although the surface area decreases with an increase in Mg/Si ratio, the impregnation contents increase. This indicates that the impregnation sites on the support are mainly on the outer surface and that magnesium oxide complexes ($-\text{Si}-\text{O}-\text{Mg}-\text{Cl}$) on the surface of the support play a role for the impregnation precursor.

3.3. Characteristics of ethylene polymerization catalyzed over various supported catalysts

Tables 3 and 4 show the results of ethylene polymerization, as catalyzed by the homogeneous metallocene catalyst (Cp_2ZrCl_2), the metallocene supported catalyst ($\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}$ or $\text{MAO}/\text{Support}$), the hybrid-supported catalysts ($\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}$ or $\text{MAO}/\text{Support}$), and the Ziegler–Natta-supported catalyst ($\text{TiCl}_4/\text{TiBAL}$ or $\text{MAO}/\text{Support}$). In comparing Mw and MWD of the polymer produced by the homogeneous metallocene catalyst with those by the metallocene supported catalyst, the Mw increased and the MWD was slightly broadened from the homogeneous to the

supported metallocene catalyst. The main reason for this behaviour is the fact 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 Mw and different polymer chains (broad MWD), compared with the homogeneous metallocene catalyst [12]. In addition, these data suggest that the impregnated catalyst remains attached to the support during the polymerization. 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 Mw of polymer.

Since the hybrid catalysts have two different active sites, the polymers produced via the hybrid catalysts with the MAO cocatalyst represent two melting peaks, resulting from catalysis by Cp_2ZrCl_2 and TiCl_4 , respectively. However, the bimodality patterns over the hybrid catalysts are different from one another, as shown in

Table 2
Characteristics of SiO_2 prepared by the sol–gel method and various catalysts

Mg/Si (mol/mol)	Supports and catalysts	Surface area (m^2/g)	Si, Mg (mmol)	Surface ratio Si:Mg:Cl (mmol)	Al (mmol)	Zr (mmol)	Ti (mmol)
0.1	SiO_2	175.0	14.8, 0.810	28.8:1.19:4.54	–	–	–
	$\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$	–	–	–	3.37	0.0406	–
	$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$	–	–	–	3.24	0.0252	0.347
	$\text{TiCl}_4/\text{MAO}/\text{SiO}_2$	–	–	–	3.21	–	0.432
0.3	SiO_2	99.9	14.3, 2.02	23.0:2.14:8.49	–	–	–
	$\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$	–	–	–	4.46	0.0855	–
	$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$	–	–	–	4.07	0.0493	0.413
	$\text{TiCl}_4/\text{MAO}/\text{SiO}_2$	–	–	–	4.11	–	0.559
0.5	SiO_2	74.7	13.7, 3.21	20.2:2.88:10.21	–	–	–
	$\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$	–	–	–	6.21	0.106	–
	$\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$	–	–	–	5.60	0.0658	0.489
	$\text{TiCl}_4/\text{MAO}/\text{SiO}_2$	–	–	–	5.27	–	0.637

Table 3
Analytical data on the polyethylene produced by MgCl₂ supported catalysts

Catalysts	Cocatalyst	Mole ratio (Al/[Metal])	Activity ^a	Tm (°C)	Xc (%) ^b	Mw (× 10 ⁻⁵)	MWD
Cp ₂ ZrCl ₂	MAO	Al/Zr = 3000	34532.2	124.9	78.9	0.15	2.1
Cp ₂ ZrCl ₂ /TiBAL/MgCl ₂ · 4CH ₃ OH	–	–	–	–	–	–	–
	MAO	Al/Zr = 3000	2535.7	127.8	73.8	0.46	3.4
TiCl ₄ /Cp ₂ ZrCl ₂ /TiBAL/MgCl ₂ · 4CH ₃ OH	MAO	Al/Zr = 3000	15720.6	126.4/135.3	68.9	6.81	9.7
	MAO	Al/Zr = 3000	16833.5	134.8	64.8	7.04	6.8
	TEA	Al/Ti = 50	–	–	–	–	–
	TEA	Al/Ti = 300	893.8	135.1	65.4	7.69	5.9
TiCl ₄ /TiBAL/MgCl ₂ · 4CH ₃ OH	–	–	–	–	–	–	–
	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: T_p = 70°C; P_{C₂H₄} = 1.3 atm; P_{H₂} = 0.2 atm.

^aActivity: kg-HDPE/mol-[Metal] atm h.

^bCrystallinity: Xc (%) = 100(ΔHm/ΔHm*); ΔHm* = 282.84 J/g.

Fig. 3. For the hybrid catalysts supported on the recrystallized MgCl₂, the polyethylene portion produced by the Ziegler–Natta catalyst is more dominant than that by the metallocene catalyst. In contrast to this pattern, for the hybrid catalysts supported on SiO₂, the polyethylene portion produced by the metallocene catalyst is

more dominant than that by the Ziegler–Natta catalyst. This is due to the higher activity of the Ziegler–Natta catalyst vis-à-vis that of the metallocene catalyst over the recrystallized MgCl₂, and that the activity of the metallocene catalyst is more active vis-à-vis that of the Ziegler–Natta catalyst over the SiO₂.

Table 4
Analytical data on the polyethylene produced by silica supported catalysts with respect to Mg/Si = 0.5

Catalysts	Cocatalyst	Mole ratio (Al/[Metal])	Activity ^a	Tm (°C)	Xc (%) ^b	Mw (× 10 ⁻⁵)	MWD
Cp ₂ ZrCl ₂	MAO	Al/Zr = 3000	34532.2	124.9	78.9	0.15	2.1
Cp ₂ ZrCl ₂ /MAO/SiO ₂	–	–	–	–	–	–	–
	MAO	Al/Zr = 3000	3174.5	132.0	71.4	0.53	2.6
TiCl ₄ /Cp ₂ ZrCl ₂ /MAO/SiO ₂	MAO	Al/Zr = 3000	819.4	132.7/139.6	65.2	2.28	4.5
	MAO	Al/Zr = 3000	689.5	131.0/139.6	62.5	4.86	21.2
	TEA	Al/Ti = 50	–	–	–	–	–
	MAO	Al/Zr = 3000	514.7	129.3/140.3	62.0	6.90	14.8
	TEA	Al/Ti = 100	–	–	–	–	–
	MAO	Al/Zr = 3000	375.6	126.8/140.0	56.8	7.54	6.2
	TEA	Al/Ti = 300	–	–	–	–	–
	TEA	Al/Ti = 300	231.4	139.2	58.9	7.21	5.8
TiCl ₄ /MAO/SiO ₂	–	–	–	–	–	–	–
	TEA	Al/Ti = 300	210.2	137.7	60.4	7.40	6.5

Conditions: T_p = 70°C; P_{C₂H₄} = 1.3 atm; P_{H₂} = 0.2 atm.

^aActivity: kg-HDPE/mol-[Metal] atm h.

^bCrystallinity: Xc (%) = 100(ΔHm/ΔHm*); ΔHm* = 282.84 J/g.

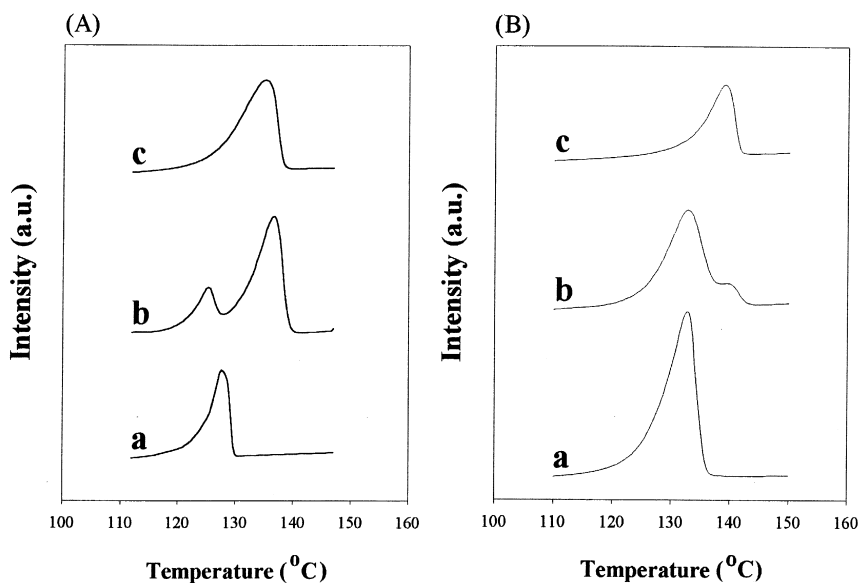


Fig. 3. DSC thermograms of polyethylene produced by various catalysts: (A) MgCl_2 -supported catalysts and (B) SiO_2 -supported catalysts. (A): (a) $\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, MAO (Al/Zr = 3000); (b) $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, MAO (Al/Zr = 3000); (c) $\text{TiCl}_4/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, TEA (Al/Ti = 300). (B): (a) $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$, MAO (Al/Zr = 3000); (b) $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$, MAO (Al/Zr = 3000); (c) $\text{TiCl}_4/\text{MAO}/\text{SiO}_2$, TEA (Al/Ti = 300).

The variation of GPC profiles is similar to that of the DSC thermograms, as shown in Fig. 4. The MWD of polyethylene produced on the hybrid catalysts exhibits a bimodal pattern. One peak in the low-Mw region is the result of the catalysis from Cp_2ZrCl_2 , and the other peak of the high-Mw region is from TiCl_4 . Moreover, the position of the two peaks is coincidental with that of the individual polyethylene peak

produced by the metallocene and Ziegler–Natta supported 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.

The hybrid catalysts have two different active sites, if MAO and TEA are simultaneously used as cocatalysts, their hybrid characteristics are

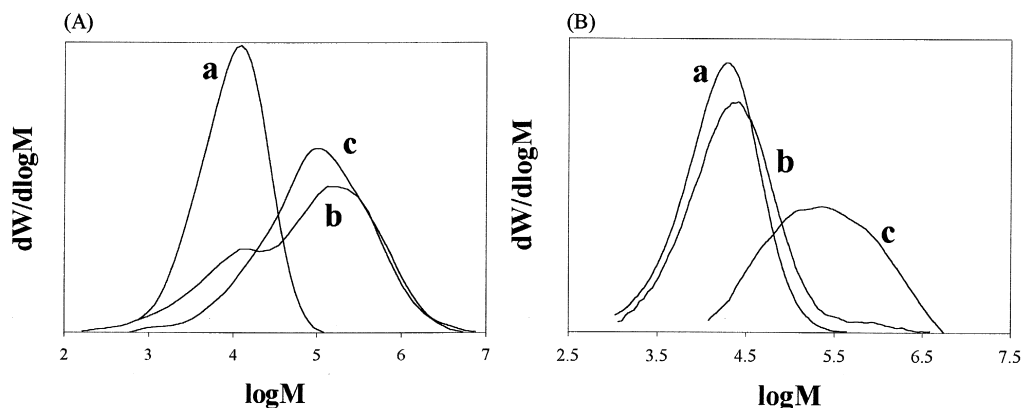


Fig. 4. GPC profiles of polyethylene produced by various catalysts: (A) MgCl_2 -supported catalysts and (B) SiO_2 -supported catalysts. (A): (a) $\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, MAO (Al/Zr = 3000); (b) $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, MAO (Al/Zr = 3000); (c) $\text{TiCl}_4/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, TEA (Al/Ti = 300). (B): (a) $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$, MAO (Al/Zr = 3000); (b) $\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$, MAO (Al/Zr = 3000); (c) $\text{TiCl}_4/\text{MAO}/\text{SiO}_2$, TEA (Al/Ti = 300).

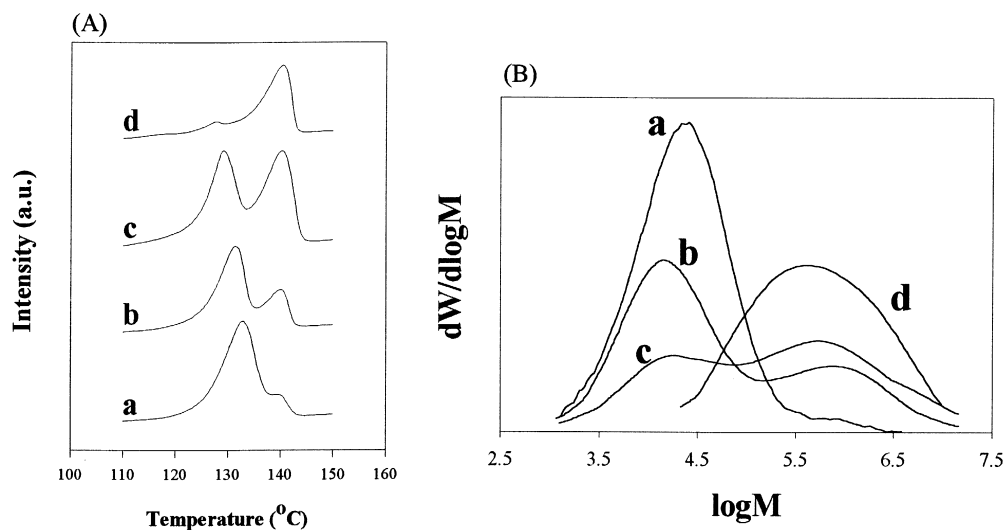


Fig. 5. DSC thermograms and GPC profiles of polyethylene produced by silica-supported hybrid catalysts ($\text{TiCl}_4/\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$) with MAO and TEA cocatalyst: (a) MAO (Al/Zr = 3000); (b) MAO (Al/Zr = 3000) and TEA (Al/Ti = 50); (c) MAO (Al/Zr = 3000) and TEA (Al/Ti = 100); (d) MAO (Al/Zr = 3000) and TEA (Al/Ti = 300).

more clearly observed, because TEA is known to be a selective poison for the active site of the metallocene catalyst [13]. For the case of the hybrid catalysts supported on SiO_2 , the bimodality could be adjusted by using these two cocatalysts, MAO and TEA. As shown in Fig. 5(A), two characteristic peaks, which represent the melting points of the polyethylene species resulting from each TiCl_4 and Cp_2ZrCl_2 , were clearly observed. The peak around 140°C increased with increasing amounts of TEA. On the contrary, the peak around 130°C decreased with increasing amounts of TEA. This is due to

the fact that alkylaluminum compounds act as selective poisons for the metallocene catalyst because aluminum alkyls form alkyl aluminum chloride complexes with the active zirconocene species, and, as a result, the amount of active zirconocene is reduced [13]. The variation of GPC profiles is similar to that of the DSC thermograms as shown in Fig. 5(B). The positions of the two peaks via the hybrid catalysts are consistent with those of the polymers produced by metallocene and Ziegler–Natta catalysts, respectively. It is noteworthy that this variation in modality affects the Mw as well as

Table 5

Analytical data on the polyethylene produced by mixed catalysts with respect to Ti/Zr ratio: $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ and $\text{TiCl}_4/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$

Ti/Zr (mol/mol)	Cocatalyst (MAO)	Activity ^a	Tm (°C)	Xc (%) ^b	Mw ($\times 10^{-5}$)	MWD
1/–	Al/Ti = 2000	7996.3	137.8	64.5	8.25	6.5
1/2	Al/[Zr + Ti] = 2000	9874.8	129.5/137.7	68.9	7.27	9.8
1/5	Al/[Zr + Ti] = 2000	7610.7	130.0/137.7	68.6	6.74	13.8
1/10	Al/[Zr + Ti] = 2000	6789.1	129.5/136.2	70.1	4.58	11.9
1/20	Al/[Zr + Ti] = 2000	4563.3	129.8/135.2	69.7	2.77	7.7
–/1	Al/Zr = 2000	2214.9	128.9	75.3	0.52	2.7

Conditions: $T_p = 70^\circ\text{C}$, $P_{\text{C}_2\text{H}_4} = 1.3 \text{ atm}$, $P_{\text{H}_2} = 0.2 \text{ atm}$.

^aActivity: kg-HDPE/mol-[Metal] atm h.

^bCrystallinity: $X_c (\%) = 100(\Delta\text{Hm}/\Delta\text{Hm}^*)$, $\Delta\text{Hm}^* = 282.84 \text{ J/g}$.

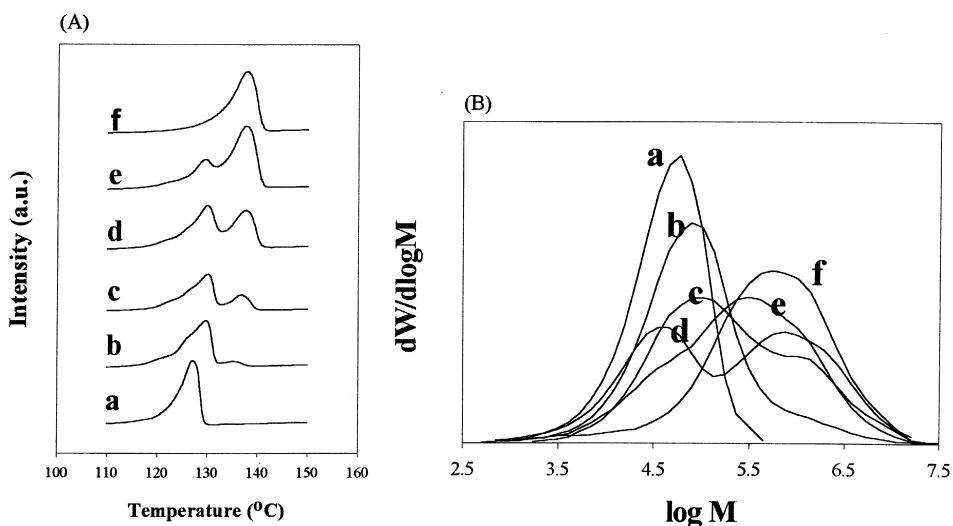


Fig. 6. DSC thermograms and GPC profiles of polyethylene produced by mixed catalysts with MAO cocatalyst: (a) $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$, $\text{Al}/\text{Zr} = 2000$. $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ and $\text{TiCl}_4/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$: (b) $\text{Ti}/\text{Zr} = 1/20$, $\text{Al}/[\text{Zr} + \text{Ti}] = 2000$; (c) $\text{Ti}/\text{Zr} = 1/10$, $\text{Al}/[\text{Zr} + \text{Ti}] = 2000$; (d) $\text{Ti}/\text{Zr} = 1/5$, $\text{Al}/[\text{Zr} + \text{Ti}] = 2000$; (e) $\text{Ti}/\text{Zr} = 1/2$, $\text{Al}/[\text{Zr} + \text{Ti}] = 2000$; (f) $\text{TiCl}_4/\text{TiBAL}/\text{MgCl}_2 \cdot 4\text{CH}_3\text{OH}$, $\text{Al}/\text{Ti} = 2000$.

the MWD, and can be controlled by varying the cocatalyst ratio.

In addition, the Mw and the MWD can be controlled by the use of the Ziegler–Natta/Metallocene mixed catalysts. Table 5 shows the results of the polymers produced by the mixed catalysts. With MAO cocatalyst, both the metallocene and the Ziegler–Natta catalysts are active, and, in this case, the bimodality can be varied with the mole ratio of catalysts, Cp_2ZrCl_2 to TiCl_4 . As the mole ratio of TiCl_4 to Cp_2ZrCl_2 increases, so the Mw increases due to the higher Mw produced by TiCl_4 , and the MWD varies with respect to the variation in modality. As shown in Fig. 6, the portion of polyethylene produced by the Ziegler–Natta catalyst increases with increasing levels of TiCl_4 , and the variation of peak intensity in GPC showed the same tendency in the DSC thermograms.

4. Conclusions

Hybrid catalysts appear to be compatible on the supports examined herein, and produce the

blend of polymers, which are characteristics of each of the individual catalysts. The resulting polymers showed bimodal patterns, as evidenced by DSC and GPC analyses, suggesting that the hybrid catalysts acted as individual active species over the support. However, the bimodality patterns differ with the type of support, and, for the case of hybrid catalysts over SiO_2 , the bimodality patterns can be varied with the TEA to MAO cocatalyst ratio. In addition, the Ziegler–Natta/Metallocene mixed catalysts are capable of producing a blend of polymers, and Mw and MWD can be controlled by varying the catalyst ratio.

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