Polymerization of Ethylene and Ethylene/1-Hexene over Ziegler-Natta/Metallocene Hybrid Catalysts Supported on SiO$_2$ Prepared by a Sol-Gel Method

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ABSTRACT: A silica support for use in olefin polymerization was prepared by the gelation of a stable, colloidal phase of silica sol using a MgCl$_2$ solution as the initiator. The Ziegler-Natta/Metallocene hybrid catalysts prepared using this support exhibited characteristics of both Ziegler-Natta and metallocene catalysts. The polymers produced by the hybrid catalysts showed a bimodal molecular weight distribution pattern and two different melting points, corresponding to products arising from each catalyst. This suggests that the hybrid catalysts acted as individual active species and produced a blend of polymers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2318–2326, 2000

Key words: silica support; metallocene catalyst; Ziegler-Natta catalyst; hybrid catalysts; polymerization; ethylene; 1-hexene

INTRODUCTION

Metallocene catalyst systems, which were discovered by Kaminsky and Sinn, are generally viewed as the next generation of catalysts for olefin polymerization.[1] These systems are highly active with respect to olefin polymerization reactions, and are capable of producing polymers with special properties that cannot be achieved via Ziegler-Natta catalyst systems.[2,3] Metallocene catalyst systems are, essentially, homogeneous systems, and the majority of studies have concentrated on solution-phase processes. For metallocene catalysts to be used in slurry or gas phase processes, an impregnation procedure on a support is necessary. In addition, because most of the commercial polymerization processes use heterogeneous catalyst systems, the preparation of heterogeneous metallocene catalysts is a prerequisite for the prevailing processes. A metallocene catalyst can be converted to a heterogeneous system in two ways. The first involves the impregnation of the metallocene catalyst on a suitable support, such as SiO$_2$, Al$_2$O$_3$, Zeolite, etc.,[4-6] and the second involves the impregnation of both a metallocene and a Ziegler-Natta catalyst in a hybrid form. Such hybrid catalysts have the potential for taking advantage of the properties of both metallocene and Ziegler-Natta catalysts. Although metallocene catalysts have the advantages of high activity and special polymer properties, the polymers produced via these catalysts have a very narrow molecular weight distribution (MWD). In polymer processing, both molecular weight and MWD are important factors, because they play a major role as determinants of mechanical and rheological properties, respectively.[7] On the one hand, polyethylenes with a narrow MWD lead to

products with high impact resistance and a higher resistance to environmental stress cracking. Conversely, those with a broad MWD show greater melt flowability at high shear rates. These properties are very important in terms of blowing and extrusion techniques.[8] The narrow MWD of polymers produced via the use of metallocene catalysts can be broadened by preparing Ziegler-Natta/Metallocene hybrid catalysts, because of the relatively higher molecular weight of polymers derived from the Ziegler-Natta component. Hybrid catalysts would be expected to enhance the polymer processability and to be utilized in prevailing processes without significant process modification.

The present study reports on the development of a new type of silica support, which was prepared by the polymerization of the colloidal phase of a stable sol using a $MgCl_2$ solution as an initiator in a chemical reaction between the stable sol (—Si—O$^-$Na$^+$) and Mg^{2+} cations. This silica support would be expected to be useful for the impregnation of both Ziegler-Natta and metallocene catalysts. The polymerization of ethylene and ethylene/1-hexene was carried out using this system to investigate the characteristics of the hybrid catalysts.

EXPERIMENTAL

Materials

High purity ethylene and N_2 (Sinyang Gas Products, Seoul, Korea) were purified by sequential passage through columns containing 5 Å molecular sieves (Kokusan Chemical Works, Tokyo, Japan) and anhydrous P_2O_5 (Yakuri Chemicals, Osaka, Japan). Toluene (Oriental Chemical Industry, Seoul, Korea) and 1-hexene (Carlo Erba, Milano, Italy) were purified by distillation over elemental sodium. $MgCl_2$ (Aldrich Chemical Company, Milwaukee, WI), colloidal SiO_2 (LUDOX HS-40, Dupont), Cp_2ZrCl_2 (Strem Chemicals, Newburyport, MA), $TiCl_4$ (Aldrich), triethylaluminium (TEA; Aldrich), and methylaluminoxane in toluene, type 4 (MAO; 6.92 Al wt %, Akzo Chemicals, Illinois) were used without further purification.

Preparation of Support and MAO-Treated Support

$MgCl_2$ was dissolved in 100 mL of distilled water. The resulting solution was then introduced into a 4-L reactor containing a 2.5 L of corn oil and stirred at 2000 rpm for the solution to be uniformly dispersed in the medium. Eighty milliliters of colloidal SiO_2 was then introduced to this slurry to initiate gelation between the stable silica sol and Mg^{+2}. The particles separated from the solution were washed and dried at 80°C for 24 h (SiO_2). One hundred milliliters of toluene was introduced into a glass reactor, and 5 g of support was then suspended in it, followed by the addition of a 100 mmol MAO solution at 0°C. The mixture was stirred at 0, 20, 40, and 60°C for 30 min each and then stirred at 80°C for 2 h. The mixture was then washed seven times with 100 mL of toluene at 80°C for 30 min and dried under vacuum (MAO/SiO_2).

Catalyst Preparation

Two grams of MAO-treated support was suspended in 100 mL of toluene and reacted with 0.30 g Cp_2ZrCl_2 at 50°C for 2 h and then washed nine times with 100 mL of toluene at 50°C for 30 min (Cp_2ZrCl_2/MAO/SiO_2). $TiCl_4$ (2.0 mL) was then introduced into this slurry. The mixture was stirred for 2 h at 70°C, and washed nine times with 100 mL of toluene at 70°C for 30 min ($TiCl_4$/Cp_2ZrCl_2/MAO/SiO_2). The support was reacted with 5 mL of $TiCl_4$ at 70°C for 2 h and then washed nine times with 100 mL of toluene at 70°C for 30 min ($TiCl_4$/MAO/SiO_2).

Characterization

The morphology of the support was examined by means of scanning electron microscopy (SEM) (JEOL JSM-840A). The elemental content ratio on the surface of the support was measured by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) (JEOL JSM-840A). The surface area and pore volume were determined by means of an N_2-BET analyzer (Micromeritics ASAP-2000). The Al, Ti, and Zr contents of the catalysts were determined via the use of an inductively coupled plasma (ICP)(VG PQ2-Turbo, VG elemental). X-ray fluorescence (XRF) (Shimazu-1700) was used to determine the Mg and Si content of the support. Polymer analysis by differential scanning calorimetry (DSC) (Dupont V 4.0B) was carried out at a heating rate of 10°C/min. Molecular weights and molecular weight distribution were determined by gel permeation chromatography (GPC) (PL-210, Poly-

mer Laboratories Ltd.) at 160°C with 1,2,4-trichlorobenzene as a solvent. For the analysis of the polyethylene and ethylene/1-hexene copolymer, the columns were calibrated universally with nar-
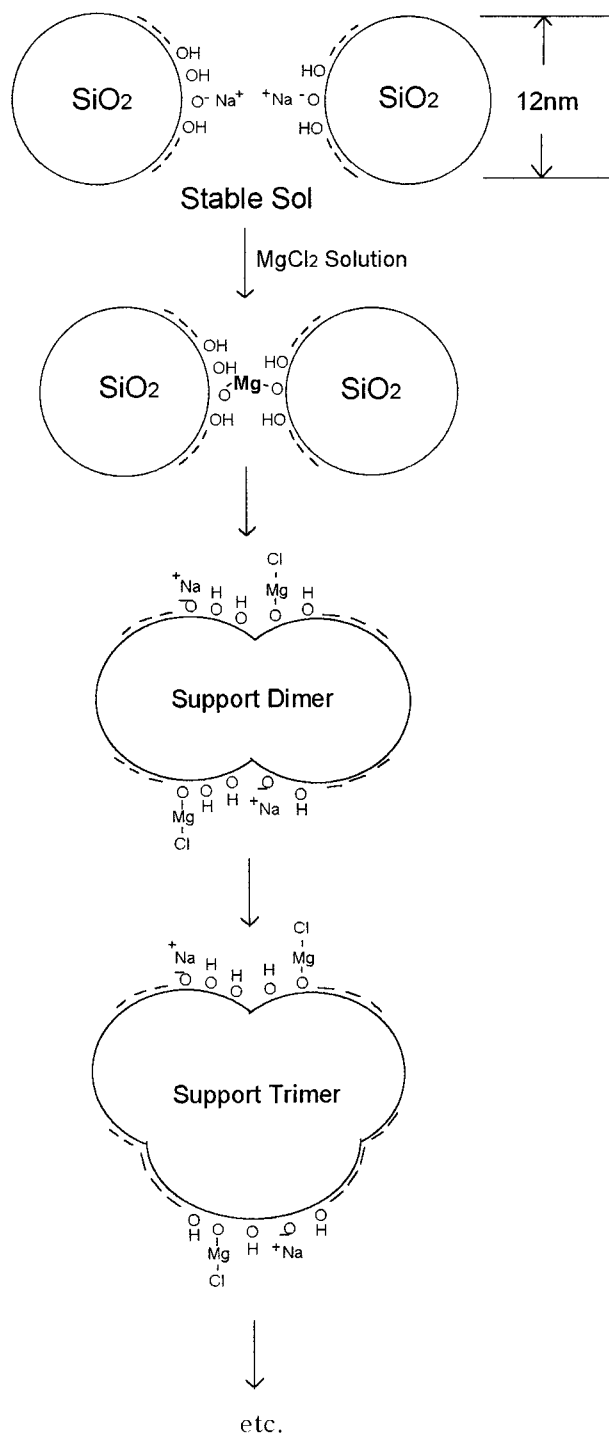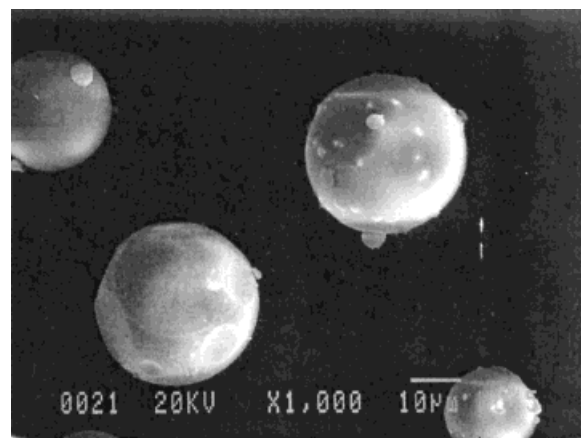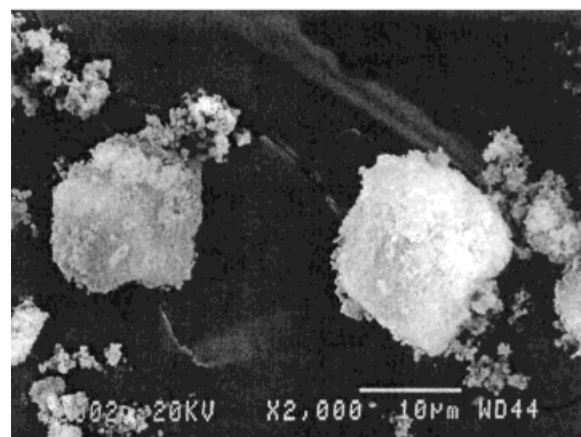

Figure 1 Proposed mechanism of the reaction between colloidal SiO_2 and $MgCl_2$ solution.

(a)

(b)

Figure 2 SEM photographs of the support prepared at 2000 r.p.m. with respect to Mg/Si = 0.3: (a) SiO_2 (×1000); (b) MAO/SiO_2 (×2000).

row molecular weight polystyrenes. The results are not absolute, but relative. The 1-hexene content in the copolymer was measured by Fourier transform infrared spectroscopy (FTIR) (Nicolet Impact-410).[9]

Polymerization of Ethylene and Ethylene/1-Hexene

Toluene (300 mL) and a 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

Table I   Characteristics of the Silica Support

Mg/Si (mol/mol)	Surface Area (m^2/g)	Pore Volume (cc/g)	Si, Mg Content (wt %)	Surface Ratio Si:Mg:Cl (wt %)
0.1	175.0	0.580	Si:41.5 Mg:1.97	81.0:2.9:16.1
0.3	99.9	0.163	Si:40.1 Mg:4.92	64.7:5.2:30.1
0.5	74.7	0.120	Si:38.6 Mg:7.81	56.8:7.0:36.2

ethylene supply and then, ethylene was fed into the reactor at a constant pressure. In the copolymerization reactions, ethylene was continuously supplied with the toluene solution which contained 1-hexene. The polymerization reaction was initiated by introducing the catalyst suspension into the reactor with a syringe. The polymerization 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 ethylene consumed, which was measured with a mass flowmeter.

RESULTS AND DISCUSSION

Characteristics of the Silica Support

Figure 1 shows a proposed mechanism for the formation of the silica support. Particles of the colloidal sol used in the preparation of the support were about 12 nm in diameter. These particles have negative charges on their surfaces, which serve to suppress the gelation of particles.[10] When a MgCl$_2$ solution is added to this stable sol, the soluble magnesium salt neutralizes the neg-

ative charge from the surface of the stable sol and the silica undergoes gelation via dimerization, trimerization, and finally, polymerization. As shown in Figure 2(a), the produced support has a spherical morphology with a particle diameter of about 20–30 μm. Table I shows the characteristics of the support. The supports were prepared at different Mg/Si ratios at 2000 rpm. The surface area and the pore volume decrease with increasing ratios of Mg/Si, but both the Mg content and the relative surface ratio of Mg increase because of the reaction between the silica sol and the dissolved magnesium salt. The difference of the relative weight ratio of Mg/Si between in the bulk and on the surface of the support was from 30 to 60 (wt %/wt %), depending on the reaction ratio. This suggests that magnesium is reasonably well distributed throughout the inner and outer portions of the supports. The relative ratio of Mg to Cl on the surface of the support increased with increasing ratios of Mg/Si. This is consistent with hydroxyl groups on the surface of the colloidal silica interacting with Mg^{+2} during the formation of the support, generating magnesium oxide complexes (—Si—O—Mg—Cl).

Table II   Elemental Analysis of the Catalysts

Mg/Si (mol/mol)	Catalysts	Al (wt %)	Zr (wt %)	Ti (wt %)
0.1	Cp$_2$ZrCl$_2$/MAO/SiO$_2$	9.08	0.37	—
	TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/SiO$_2$	8.74	0.23	1.66
	TiCl$_4$/MAO/SiO$_2$	8.66	—	2.07
0.3	Cp$_2$ZrCl$_2$/MAO/SiO$_2$	12.03	0.78	—
	TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/SiO$_2$	10.97	0.45	1.98
	TiCl$_4$/MAO/SiO$_2$	11.10	—	2.68
0.5	Cp$_2$ZrCl$_2$/MAO/SiO$_2$	16.75	0.97	—
	TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/SiO$_2$	15.10	0.60	2.34
	TiCl$_4$/MAO/SiO$_2$	14.21	—	3.05

Table III   Analytical Data on the Polyethylene Produced over Hybrid Catalysts with Respect to Mg/Si = 0.3[a]

Catalysts	Cocatalyst	Mol Ratio (Al/[Metal])	Activity[b]	T_m (°C)	X_c (%)[c]	M_w ($\times 10^{-5}$)	MWD
Cp$_2$ZrCl$_2$/MAO/SiO$_2$	MAO	Al/Zr = 3000	1733.2	132.0	71.4	0.53	2.4
TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/SiO$_2$	MAO	Al/Zr = 3000	574.6	132.7/139.6	65.2	2.28	4.5
	MAO TEA	Al/Zr = 3000 Al/Ti = 50	481.4	131.0/139.6	62.5	4.86	28.2
	MAO TEA	Al/Zr = 3000 Al/Ti = 100	396.5	129.3/140.3	62.0	6.90	19.8
	MAO TEA	Al/Zr = 3000 Al/Ti = 300	350.6	126.8/140.0	53.8	7.34	6.2
	TEA	Al/Ti = 300	100.6	139.2	58.9	7.11	5.8
TiCl$_4$/MAO/SiO$_2$	TEA	Al/Ti = 300	77.1	137.7	60.4	7.40	6.5

[a] Conditions: T_p = 50°C; P$_{C2H4}$ = 1.3 atm; P$_{H2}$ = 0.2 atm.
[b] Activity: kg-HDPE/mol-[Metal] · atm · h.
[c] Crystallinity: Xc(%) = 100 ($\Delta H_m/\Delta H_m^*$); ΔH_m^* = 282.84 J/g.

Effect of Mg/Si Ratio on Impregnation of Catalysts

It is well known that if a metallocene catalyst is directly impregnated on the surface of the supports without any modification, the degree of im-
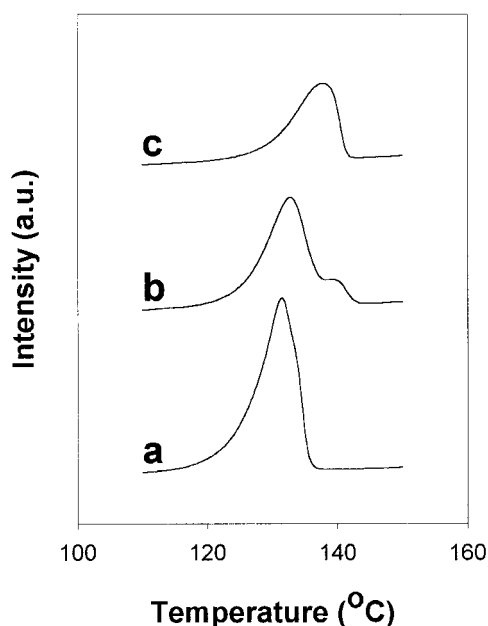

Figure 3   DSC thermograms of the polyethylene over various catalysts: (a) Cp$_2$ZrCl$_2$/MAO/SiO$_2$, MAO (Al/Zr = 3000); (b) TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/SiO$_2$, MAO (Al/Zr = 3000); (c) TiCl$_4$/MAO/SiO$_2$, TEA (Al/Ti = 300).

pregnation and catalytic activity are usually low.[11] For the impregnation of metallocene on the support surfaces, MAO is known to be a good compound for the modification of the support surface, which acts as an anchor between the metallocene catalyst and the support. Therefore, the prepared support was treated with MAO. As shown in Table II, the magnesium content affects the impregnation of both MAO and the catalysts. Although the surface area decreases with increasing ratios of Mg/Si, the impregnation content increases. This can be attributed to the fact that magnesium oxide complexes on the surface of the support play the role of an impregnation precursor. This is also consistent with the conclusion that the impregnation sites of the support are mainly on the outer surface.

In Figure 2(b), the particle size of the support treated with MAO is smaller than that of the nontreated support, as shown in Figure 2(a). This means that the support was fractured by the reaction between the support and MAO, and in addition, that the surface of the MAO-treated support is more heterogeneous than that of the nontreated support.

Polymerization of Ethylene and Ethylene/1-Hexene

Table III shows the results of ethylene polymerization with the metallocene supported catalyst (Cp$_2$ZrCl$_2$/MAO/SiO$_2$), the hybrid catalysts (TiCl$_4$/

$Cp_2ZrCl_2/MAO/SiO_2$) and the Ziegler-Natta supported catalyst ($TiCl_4/MAO/SiO_2$). The activity decreases from the metallocene supported catalyst to the Ziegler-Natta supported catalyst due to the relatively low activity characteristics of the latter catalyst. 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 the melting temperature increases in proportion to the molecular weight of polymer. As shown in Figure 3, the polymers produced via the use of hybrid catalysts showed two melting temperatures, which overlapped, in part, the region of polymer produced with the metallocene catalyst and, in part, that of the Ziegler-Natta catalyst. This suggests that the hybrid catalysts produced a blend of polymers, each of which is produced via polymerization by one of the catalysts. In this case, the polyethylene portion produced by the metallocene cata-
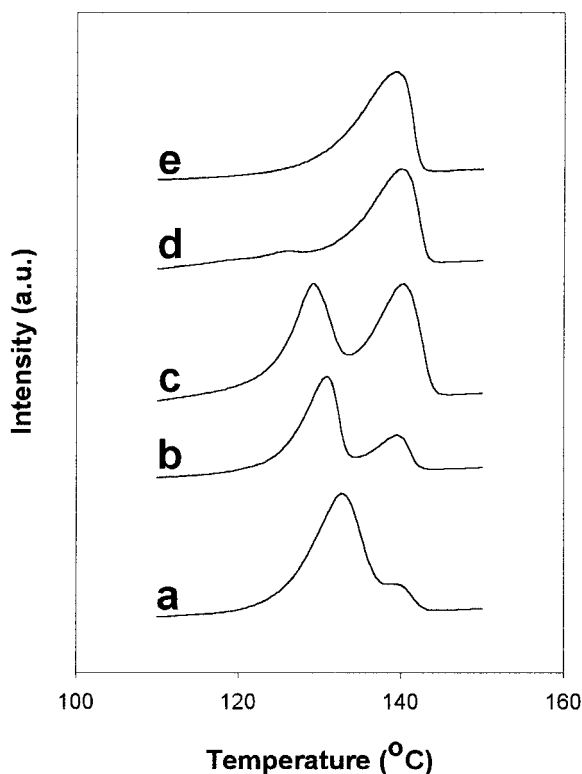

Figure 5 Activity profiles of polyethylene over various catalysts: (●) $Cp_2ZrCl_2/MAO/SiO_2$, MAO (Al/Zr = 3000); (■) $TiCl_4/Cp_2ZrCl_2/MAO/SiO_2$; MAO (Al/Zr = 3000); (▲) $TiCl_4/MAO/SiO_2$, TEA (Al/Ti = 300).

Figure 4 DSC thermograms of polyethylene over hybrid catalysts ($TiCl_4/Cp_2ZrCl_2/MAO/SiO_2$): (a) MAO (AlZr = 3000); (b) MAO and TEA (Al/Ti = 50); (c) MAO and TEA (Al/Ti = 100); (d) MAO and TEA (Al/Ti = 300); (e) TEA (Al/Ti = 300).
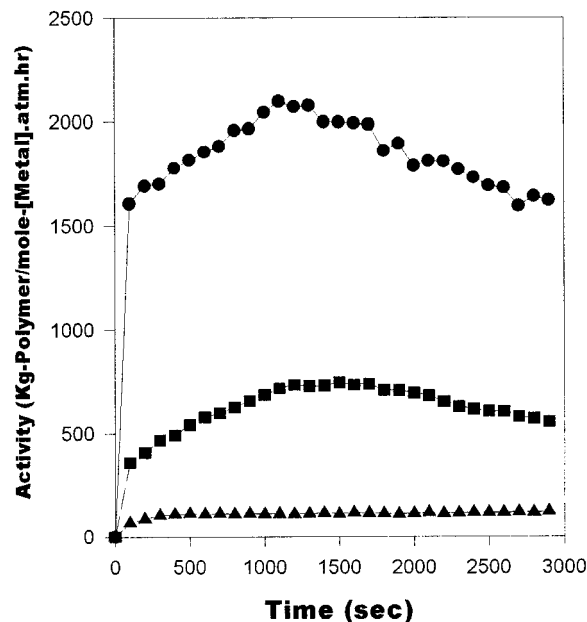
lyst is more dominant than that by the Ziegler-Natta catalyst, although the content of $TiCl_4$ is higher than that of Cp_2ZrCl_2, as shown in Table II. This is due to the higher activity of the metallocene catalyst vis-à-vis that of the Ziegler-Natta catalyst over the silica support.

Because hybrid catalysts have two different active sites on the support, if MAO and TEA are simultaneously used as cocatalysts, hybrid effects would be more clearly observed. As shown in Figure 4, two characteristic peaks representing the melting points resulting from each Cp_2ZrCl_2 and $TiCl_4$ were clearly observed. The peak intensity around 140°C, corresponding to polyethylene produced by $TiCl_4$, increased with increasing amounts of TEA. On the contrary, the peak around 130°C, which corresponds to Cp_2ZrCl_2, decreased with increasing TEA. This can be attributed to the fact that alkyl aluminum forms a complex with the active zirconium, occupies vacant coordinate sites and, finally, reduces the number of active sites.[12] Although the activity is decreased in proceeding from the metallocene supported catalyst to the Ziegler-Natta supported catalyst, the activity persists for periods of up to an hour, as shown in Figure 5, suggesting that the supported catalysts were stabilized to a con-

Table IV Analytical Data on the Ethylene/1-Hexene Copolymer Produced over Hybrid Catalysts with Respect to Mg/Si = 0.5[a]

Catalysts	Cocatalyst	Mole Ratio (Al/[Metal])	Activity[b]	T_m(°C)	ΔH_m	M_w (×10^{-5})	MWD	1-Hexene (mol%)
Cp_2ZrCl_2/MAO/SiO_2	MAO	Al/Zr = 3000	1812.7	113.3	144.4	0.49	2.7	3.5
$TiCl_4$/Cp_2ZrCl_2/MAO/SiO_2	MAO	Al/Zr = 3000	570.4	128.5/136.7	177.9	1.81	4.3	2.5
	MAO TEA	Al/Zr = 3000 Al/Ti = 300	450.7	126.0/136.8	166.9	4.81	35.9	2.4
	MAO TEA	Al/Zr = 3000 Al/Ti = 600	409.0	123.0/137.8	149.6	6.35	24.2	2.0
	MAO TEA	Al/Zr = 3000 Al/Ti = 1000	325.5	137.8	159.6	7.69	5.6	1.8
	TEA	Al/Ti = 300	92.4	138.2	156.1	7.51	6.7	1.5
$TiCl_4$/MAO/SiO_2	TEA	Al/Ti = 300	87.7	133.5	166.6	7.30	6.6	1.6

[a] Conditions: T_p = 50°C; P_{C2H4} = 1.3 atm; P_{H2} = 0.2 atm.
[b] Activity: kg-[Ethylene/1-Hexene]/mole-[Metal] · atm · h.

siderable extent. Generally speaking, a reduction in catalytic activity with time is a characteristic of $MgCl_2$ supported Ziegler-Natta catalysts.[13] How-

Figure 6 DSC thermograms of ethylene/1-hexene co-polymer over various catalysts: (a) Cp_2/$ZrCl_2$/MAO/SiO_2, MAO (Al/Zr = 3000); (b) $TiCl_4$/Cp_2ZrCl_2/MAO/SiO_2, MAO (Al/Zr = 3000); (c) $TiCl_4$/MAO/SiO_2, TEA (Al/Ti = 300).

ever, the activity profiles of both the hybrid catalysts and Ziegler-Natta supported catalyst are maintained.

For the case of the copolymerization of ethylene with 1-hexene as shown in Table IV, the content of 1-hexene decreases in proceeding from the metallocene to the Ziegler-Natta supported catalyst. This suggests that the insertion of 1-hexene into the growing polymer chain is more effective for the case of metallocene than for the Ziegler-Natta catalyst. Figure 6 shows data on the copolymers produced by the hybrid catalysts, including the two melting temperatures. However, the melting temperature for the polymer produced via the metallocene over the hybrid catalysts is higher than that of the metallocene supported catalyst. This indicates that the insertion of 1-hexene is hindered over the hybrid catalysts, compared with the metallocene supported catalyst, and, in addition, this result is correlated with 1-hexene content in Table IV. As shown in Figure 7, similar to the tendency of the ethylene polymerization, the bimodality could be adjusted by using two cocatalyst, namely, MAO and TEA. With the increase in the ratio of TEA to MAO, the portion of polyethylene produced by the Ziegler-Natta catalyst increases. However, both the content of 1-hexene in the copolymer and the catalytic activity decrease.

Figures 8 and 9 show that the molecular weight distribution of polyethylene and copoly-
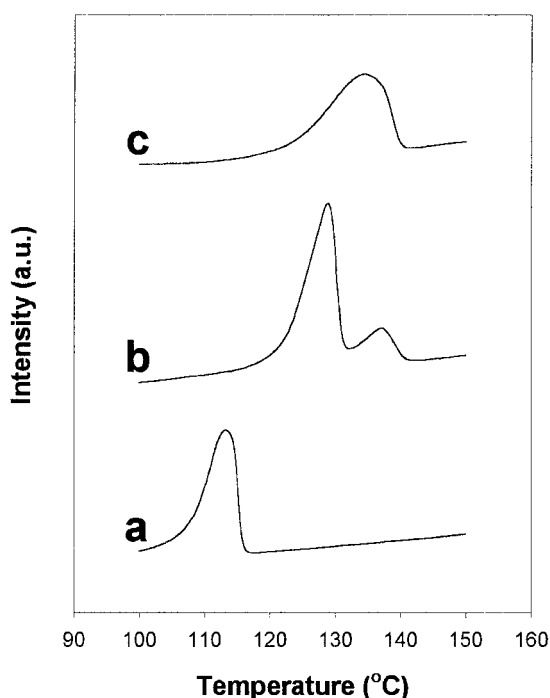
Figure 7 DSC thermograms of ethylene/1-hexene copolymer over hybrid catalysts (TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/ SiO$_2$): (a) MAO (Al/Zr = 3000); (b) MAO and TEA (Al/Ti = 300); (c) MAO and TEA (Al/Ti = 600); (d) MAO and TEA (Al/Ti = 1000); (e) TEA (Al/Ti = 300).

Figure 8 GPC profiles of polyethylene over various catalysts: (a) Cp$_2$ZrCl$_2$/MAO/SiO$_2$, MAO (Al/Zr = 3000); TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/SiO$_2$; (b) MAO and TEA (Al/Ti = 50); (c) MAO and TEA (Al/Ti = 100); (d) TiCl$_4$/MAO/ SiO$_2$, TEA (Al/Ti = 300).
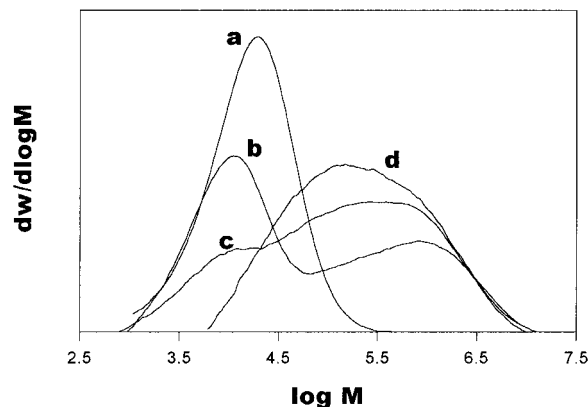
Figure 9 GPC profiles of ethylene/1-hexene copolymer over various catalysts: (a) Cp$_2$ZrCl$_2$/MAO/MAO/ SiO$_2$, MAO (Al/Zr = 3000); TiCl$_4$/Cp$_2$ZrCl$_2$/MAO/SiO$_2$; (b) MAO and TEA (Al/Ti = 300); (c) MAO and TEA (Al/Ti = 600); (d) TiCl$_4$/MAO/SiO$_2$, TEA (Al/Ti = 300).

mer via hybrid catalysts exhibits a bimodal pattern. The variation of GPC profiles is similar to that of DSC thermograms. The position of the two peaks, produced via the hybrid catalysts, is coincident with that of the polymers produced by met-
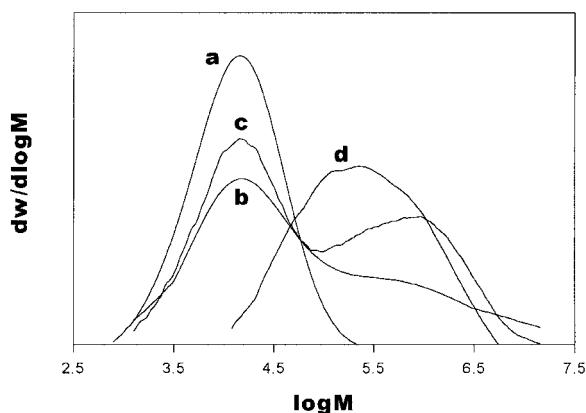
allocene or the Ziegler-Natta supported catalyst, respectively. It is noteworthy that this variation in modality affects the molecular weight as well as the molecular weight distribution, and that it can be controlled by varying the ratio of cocatalysts. For the hybrid catalysts, as the ratio of TEA to MAO increases, the MW increases due to the higher MW produced by the Ziegler-Natta catalyst, and the MWD varies with respect to the variation in the modality, as shown in Table III and IV.

Consequently, for the polymerization of both ethylene and ethylene with 1-hexene, the hybrid catalysts are capable of producing a blend of polymers, indicating that no strong chemical interaction exists between the two individual catalysts.

CONCLUSION

A silica support was prepared by the gelation of a colloidal silica sol using a MgCl$_2$ solution as an initiator. Magnesium was reasonably well distributed both on the surface and in the bulk of the support. The magnesium content affects the impregnation content of the catalysts. For the case of the polymerization of ethylene and ethylene/1-hexene, the polymer produced via hybrid catalysts showed two different melting points and a bimodal molecular weight distribution pattern, suggesting that the hybrid catalysts acted as individual active species and produced a blend of polymers. It is noteworthy that the relative por-

tion of polymers produced via hybrid catalysts can be controlled by varying the ratio of cocatalysts.

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