Preparation of the Ziegler–Natta/metallocene hybrid catalysts on SiO$_2$/MgCl$_2$ bisupport and ethylene polymerization

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Abstract

Ziegler–Natta and metallocene hybrid catalysts were impregnated on a bisupport prepared by the polymerization of colloidal phase of SiO$_2$ using MgCl$_2$ solution as an initiator. The prepared bisupport was modified by treatment with alkyl aluminum compounds. In terms of the treatment of the prepared bisupport, trimethylaluminum (TMA) was superior to methylaluminoxane (MAO) with respect to the stability of the metallocene catalyst. The prepared hybrid catalysts exhibited characteristics of both Ziegler–Natta and metallocene catalysts. The polyethylene produced on the hybrid catalysts showed a bimodal molecular weight distribution in GPC profile and two different melting points in differential scanning calorimetry (DSC) thermogram. © 1999 Elsevier Science B.V. All rights reserved.

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

1. Introduction

In recent years, metallocene catalysts have received considerable attention, because they exhibit a high activity for olefin polymerization and the polymers produced by these catalysts possess properties which are different from polymers produced by Ziegler–Natta catalyst systems [1–3]. The metallocene catalyst sysem is, basically, a homogeneous system and therefore, the majority of studies on the metallocene catalysts have concentrated on solution-phase processes. However, in order for a metallocene catalysts to be used in the prevailing slurry or gas phase processes, it is necessary to modify them to a supported form so that they can be utilized in heterogeneous systems. The preparation of a heterogeneous metallocene catalysts is required for the separation and processing of polymers, rather than for improvement in polymerization processes themselves [4]. In addition, since all commercial polymerization processes which involve Ziegler–Natta catalysts are used in heterogeneous systems, the preparation of heterogeneous metallocene catalysts is a prerequisite for the replacement of existing processes with a new catalyst system. A metallocene catalyst can be modified for a heterogeneous system in two possible ways. One is to impregnate the metallocene catalyst on suitable supports such as SiO$_2$, MgCl$_2$, Al$_2$O$_3$, and

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polymers. The other one is to impregnate the metallocene and Ziegler–Natta catalysts in a hybrid form. The hybrid catalysts can take advantage of the properties of both the metallocene and Ziegler–Natta catalysts. Although the metallocene catalyst has advantages, such as high activity and stereospecificity, the polymers produced via metallocene catalysts have a very narrow molecular weight distribution. A hybrid catalyst, however, would be expected to be utilized in the prevailing processes without significant process modification and also to enhance the processabililty of polymers.

In order to impregnate metallocene and Ziegler–Natta catalysts in a hybrid form on one support, a new type of bisupport composed of two components, $MgCl_2$ and SiO_2, was developed (hereafter denoted as $MgCl_2/SiO_2$). The newly tried bisupport was made by the polymerization of colloidal phase of the stable sol using $MgCl_2$ solution as an initiator. Different from alternate types of bisupports prepared by physically impregnating $MgCl_2$ on SiO_2 [5,6], the new type of bisupport can be made by chemical reaction between stable sol ($-Si-O^-Na^+$) and Mg^{2+} cation. The bisupport would be expected to be useful for the impregnation of both Ziegler–Natta and metallocene catalysts. In this study, bisupport and catalysts were characterized by inductively coupled plasma (ICP), energy dispersive spectroscopy (EDS), N_2-BET. Ethylene polymerization was carried out in order to investigate the characteristics of the hybrid catalysts.

2. Results and discussion

2.1. Characteristics of the $SiO_2/MgCl_2$ bisupport

Fig. 1 shows a plausible mechanism for the formation of the $SiO_2/MgCl_2$ bisupport. The colloidal SiO_2 used in the preparation of the bisupport is about 12 nm in diameter. Since these particles have a negative charge on their
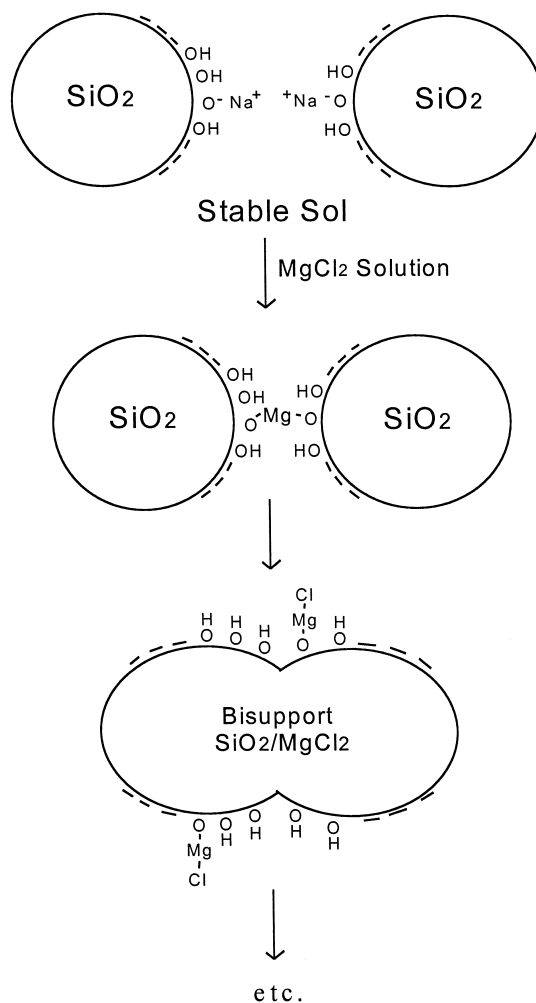

Fig. 1. Plausible mechanism of the reaction between colloidal SiO_2 and $MgCl_2$ solution.

surfaces, repulsive forces between particles suppress the agglomeration of particles to form a stable colloid [7]. If $MgCl_2$ solution is added to this stable sol, the dissolved magnesium salt discharges the negative charge from the surface of the stable sol and, finally, the SiO_2 initiates an agglomeration. Because the agglomerated $SiO_2/MgCl_2$ is formed in dispersed media, the growth of particles is limited and they are solidified within a few minutes to form the bisupport. As shown in Fig. 2, the prepared $SiO_2/MgCl_2$ bisupports show a regular particle morphology with a particle size of about 80 μm. Table 1 shows N_2-BET data of the pre-

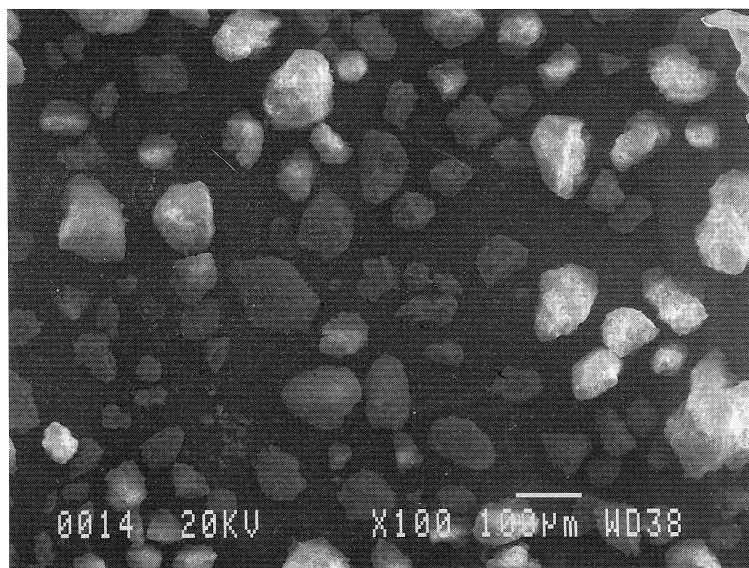Fig. 2. Scanning electron microscopy (SEM) photograph of the $SiO_2/MgCl_2$.

pared bisupport. The surface area of the $SiO_2/MgCl_2$ bisupport is slightly less than that of the original SiO_2. Considering the formation mechanism of the bisupport, as shown in Fig. 1, it is possible that $MgCl_2$ could affect the surface area and porosity of the bisupport. ICP and EDS analyses were also carried out in order to investigate the distribution of magnesium compounds in the bisupport. The mole ratio of Mg/Si in the bulk bisupport was 0.0582, while the Mg/Si mole ratio on the surface was 0.0280. This result suggests that magnesium was reasonably well distributed throughout the inner and outer portion of the prepared bisupport or that approximately the half amount of magnesium which was used for the initiator of bisupport penetrated into SiO_2 during the preparation. Also, the relative mole ratio of Si:Mg:Cl on the surface of bisupport was 89.2:2.5:8.3. It

means that chloride was bonded to the magnesium on the bisupport.

2.2. Effect of alkyl aluminum compounds on the impregnation of Cp_2ZrCl_2 on $SiO_2/MgCl_2$

It is well known that if metallocene is directly impregnated on the supports without any modification of their surfaces, the catalytic activity and the degree of impregnation are usually low [8]. For the impregnation of metallocene on the SiO_2 surfaces, methylaluminoxane (MAO) is known to be a good compound for the modification of SiO_2 surface acting as an anchor between metallocene and SiO_2. It is also known that MAO or other alkylaluminum compounds, such as TiBA (Triisobutyla-

Table 1
Characteristics of the $SiO_2/MgCl_2$ bisupport

	Surface area (m^2/g)	Pore volume (cc/g)
SiO_2	240	–
$SiO_2/MgCl_2$	210	0.97
$TMA/SiO_2/MgCl_2$	212	0.44
$MAO/SiO_2/MgCl_2$	721	0.73

Table 2
Elemental analysis of the supported catalyst

Catalyst	Element (wt.%)		
	Al	Ti	Zr
$TiCl_4/TMA/SiO_2/MgCl_2$	2.16	0.55	–
$Cp_2ZrCl_2/TMA/SiO_2/MgCl_2$	2.46	–	0.28
$Cp_2ZrCl_2/TiCl_4/TMA/SiO_2/MgCl_2$	1.74	0.44	0.095
$Cp_2ZrCl_2/MAO/SiO_2/MgCl_2$	8.58	–	2.85

luminum) and TMA (Trimethylaluminum) are also required to modify $MgCl_2$ [9,10].

In this study, the prepared $SiO_2/MgCl_2$ bisupport was treated with TMA or MAO. As shown in Table 2, the bisupport treated with MAO showed a 10-fold higher amount of Cp_2ZrCl_2 impregnation, compared to other alkylaluminum compounds. This is due to the fact that MAO-treated bisupports have a larger surface area and a higher amount of aluminum on the surface than TMA-treated bisupport. In Fig. 3, the particle size of bisupport treated with MAO or TMA is smaller than that of non-treated bisupport. It means that the agglomerated bisupport was fractured by the reaction between bisupport and alkylaluminum compounds. Especially, as shown in Fig. 3, the surface of bisupport treated with MAO is more heterogeneous than that of TMA-treated bisupport. Fig. 4 shows the activity profiles of each catalyst. The activity profile of the MAO-treated catalysts is similar to that of homogeneous Cp_2ZrCl_2, that is, it
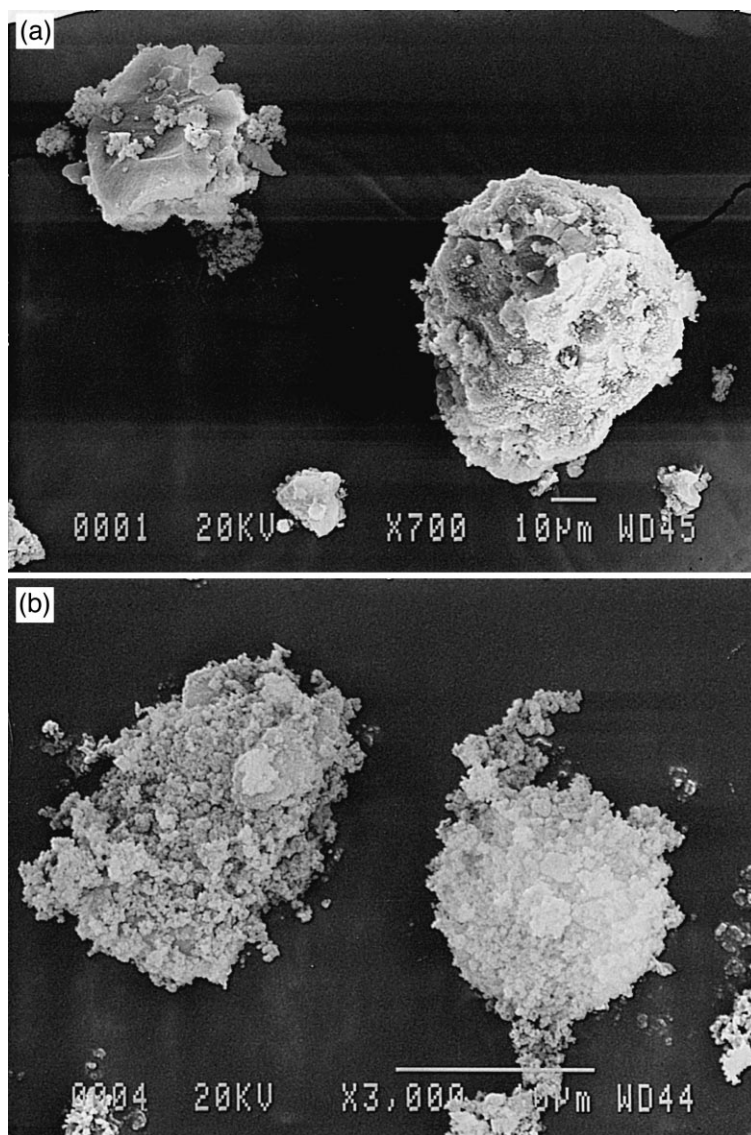

Fig. 3. SEM photographs of the $SiO_2/MgCl_2$ treated with alkylaluminum compounds: (a) $TMA/SiO_2/MgCl_2$; (b) $MAO/SiO_2/MgCl_2$.
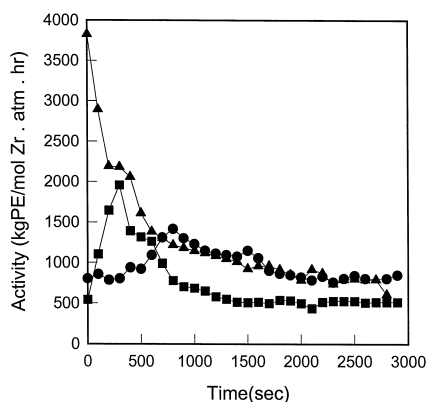
Fig. 4. Activity profile of the catalysts: ($\blacktriangle$) Cp_2ZrCl_2; ($\bullet$) Cp_2ZrCl_2 /TMA/SiO_2 /$MgCl_2$; ($\blacksquare$) Cp_2ZrCl_2 /MAO/SiO_2 / $MgCl_2$; polymerization conditions; $P_{C2H4} = 1.3$ atm; Temperature $= 50°C$; Time $= 3000$ s.

shows high activity at the initial stage and then is immediately deactivated. This suggests that the immobilized Cp_2ZrCl_2 is not stabilized well over MAO-treated bisupport surface. These activity data and other characteristics are listed in Table 3. On the contrary, the activity profile of the TMA-treated catalysts shows a slow activation–deactivation pattern. This suggests that although the immobilized amount of zirconium on the TMA-bisupport is low, the active sites are well dispersed and stabilized.

2.3. Characteristics of Cp_2ZrCl_2 / $TiCl_4$ hybrid catalysts supported on the TMA-treated bisupport

The characteristics of polyethylene formed on the hybrid catalyst which was prepared by impregnation with $TiCl_4$ followed by the impregnation with Cp_2ZrCl_2 were investigated.

Table 4
Characteristics of the produced PE over Cp_2ZrCl_2 /$TiCl_4$ hybrid catalyst on the TMA-treated bisupport

Cocatalyst	Al/Metal (mol/mol)	Activity[a]	T_m (°C)	MWD
TEA	100[c]	106.6[b]	138.8	25.1
MAO	51	663.6	131.0	3.4
			137.8	
MAO	500	817.4	130.8	2.7
MAO	1000	955.3	131.3	2.4

Polymerization conditions: $T = 60°C$, $P_{C2H4} = 1.3$ atm, $P_{H2} = 0.2$ atm.
[a]Activity: kg-PE/mol-metal. atm h.
[b]Activity: kg-PE/mol-Ti. atm h.
[c]TEA/Ti mole ratio.

The elemental analysis of the prepared catalyst and the results of ethylene polymerization experiments are shown in Tables 2 and 4, respectively. As shown in Table 4, a hybrid catalyst that has been treated with $TiCl_4$ prior to Cp_2ZrCl_2 was impregnated on the bisupport treated with TMA showed activity, even though triethylaluminum (TEA) was used as a cocatalyst.

Fig. 5 shows differential scanning calorimetry (DSC) thermograms of the polyethylene produced by Cp_2ZrCl_2/$TiCl_4$ hybrid catalysts along with the amount of MAO. When the Al/metal ratio was 500 or higher, a slight trace of peak representing the melting point of the polyethylene produced by $TiCl_4$ appeared at 137.8°C and, on the contrary, a strong peak representing that of the polyethylene produced by the active zirconocene species was observed around 131°C. This is due to the fact that the activity of the active zirconocene species is
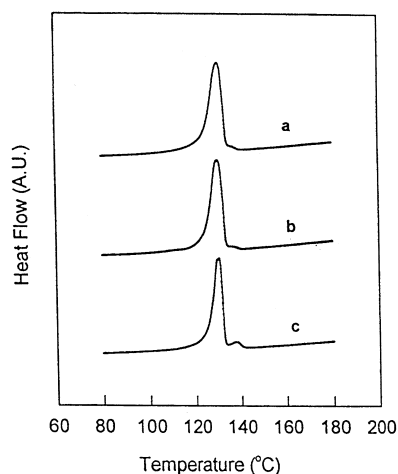
Table 3
Characteristics of the produced PE over supported catalysts

Catalyst	Cocatalyst	Al/Metal (mol/mol)	Activity[a]	T_m (°C)	MWD
Cp_2ZrCl_2	MAO	1000	1573	132.3	3.4
$TiCl_4$/TMA/SiO_2/$MgCl_2$	TEA	100	170.7	139.0	11.9
$TiCl_4$/TMA/SiO_2/$MgCl_2$	MAO	100	93.8	n.a.	n.a.
Cp_2ZrCl_2/TMA/SiO_2/$MgCl_2$	MAO	1000	1012.5	135.4	2.73
Cp_2ZrCl_2/MAO/SiO_2/$MgCl_2$	MAO	1000	733.2	134.9	3.25

Polymerization conditions: $T = 50°C$, $P_{C2H4} = 1.3$ atm, $P_{H2} = 0.0$ atm, cocatalyst = MAO, Al/Metal = 1000.
[a]Activity: kg-PE/mol-metal. atm h.
[b]Cocatalyst: TEA, Al/Metal = 100.

Fig. 5. Differential scanning calorimetry (DSC) results of polyethylene produced by Cp_2ZrCl_2 /$TiCl_4$ /TMA/SiO_2 /$MgCl_2$ catalyst: (a) MAO (Al/Mt = 1000); (b) MAO (Al/Mt = 500); (c) MAO (Al/Mt = 51).

much higher than that of $TiCl_4$. However, when the Al/metal ratio was 51, the peak at 137.8°C was distinctively observed, because the activity of the active zirconocene species is not so high with respect to that of $TiCl_4$. Such characteristics were also observed in the gel-permeation chromatography results in Fig. 6. They were consistent with the tendency of DSC results. The molecular weight distribution of the polyethylene became narrower as the amount of MAO increased and broader as it decreased. On the other hand, the molecular weight distribution of the polyethylene produced by the hybrid catalyst using TEA as a cocatalyst was broader than that of polyethylene produced by using only the $TiCl_4$ catalyst impregnated on the same bisupport. This may be due to the uniform dispersion of $TiCl_4$ by Cp_2ZrCl_2 impregnated at later stages.

Since the Cp_2ZrCl_2/$TiCl_4$ hybrid catalysts have two different active sites on the SiO_2/$MgCl_2$ bisupport, if TEA and MAO are simultaneously used as cocatalysts, their hybrid characteristics are more clearly observed. Table 5 shows the results of ethylene polymerization using both TEA and MAO as cocatalyst. The activity of the hybrid catalyst generally decreased with an increase in the amount of TEA.

As shown in Fig. 7, two characteristic peaks, representing the melting points of polyethylenes resulting from each $TiCl_4$ and Cp_2ZrCl_2 were clearly observed. The peak around 138°C corresponding to the polyethylene produced by $TiCl_4$ increased with increasing amounts of TEA. On the contrary, the peak around 131°C corresponding to Cp_2ZrCl_2 decreased with increasing amounts of TEA. It is known that TEA acts as a poison for supported Cp_2ZrCl_2 because aluminum alkyls form alkyl aluminum chloride complexes with the active zirconocene species and, as a result, the number of the active zirconocene species are reduced [11]. Although the activity of the active zirconocene species was significantly reduced, the supported Cp_2ZrCl_2 retained their activity for ethylene polymerization, suggesting that the supported Cp_2ZrCl_2 was considerably stabilized during impregnation on the bisupport. The difference of melting temperature between polymers produced by Cp_2ZrCl_2 and that by $TiCl_4$ is due to the fact that melting temperature increases in proportion to the molecular weight. The variation of peak intensity showed a same tendency to the GPC profile in Fig. 9. Fig. 8 shows that the molecular weight distribution of polyethylene produced on the hybrid catalyst exhibits a bimodal pattern. One peak in the low molecular weight region is the result of Cp_2ZrCl_2 and the other peak of
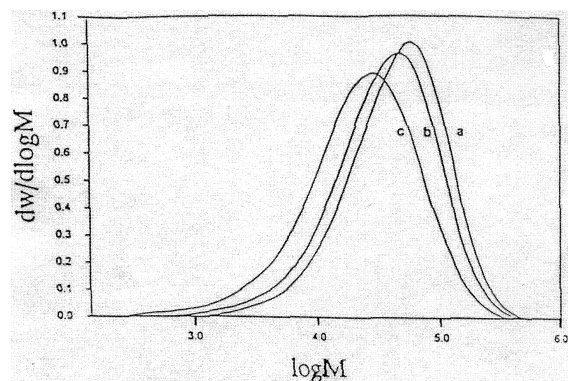

Fig. 6. Molecular weight distributions of the polyethylene produced by Cp_2ZrCl_2 /$TiCl_4$ /TMA/SiO_2 /$MgCl_2$ catalyst: (a) MAO (Al/Mt = 1000); (b) MAO (Al/Mt = 500); (c) MAO (Al/Mt = 51).

Table 5
Characteristics of the produced PE with respect to the different amount of catalysts over $Cp_2ZrCl_2/TiCl_4$ hybrid catalyst on the TMA-treated bisupport

Cocatalyst	Cocatalyst amount (mol/mol)	Activity[a]	T_m (°C)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-5}$)	MWD
TEA	100[c]	106.6[b]	138.8	3.79	9.49	25.1
MAO	500	98.2	126.7	0.97	9.22	95.5
TEA	100		138.5			
MAO	500	161.9	128.5	1.44	12.3	85.2
TEA	57		138.8			
MAO	500	139.6	128.5	10.1	7.35	73.0
TEA	29		137.6			
MAO	500[d]	663.5	131.0	1.17	0.40	3.4
			137.8			

Polymerization conditions: $T = 60°C$, $P_{C2H4} = 1.3$ atm, $P_{H2} = 0.2$ atm.
[a]Activity: kg-PE/mol-metal atm h.
[b]Activity: kg-PE/mol-Ti atm h.
[c]TEA/Ti mole ratio.
[d]MAO/Zr mole ratio.

high molecular weight region is from $TiCl_4$. Moreover, the position of the two peaks is coincident with that of the individual polyethylene peak produced by the hybrid catalysts using MAO or TEA individually.

In addition, the dependency of the molecular weight distribution of polyethylene on the amount of TEA for a fixed amount of MAO in
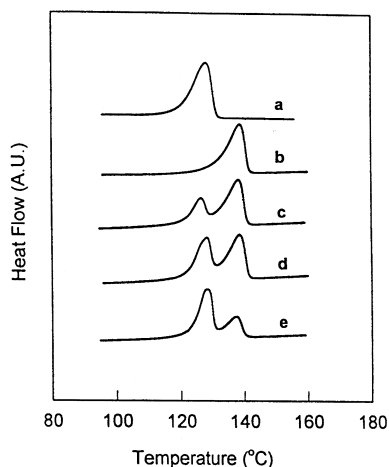
Fig. 9 is supported by the DSC data in Fig. 7. The larger the amount of TEA used, the more the active zirconocene species poisoned so that the characteristic peak of polyethylene produced by Cp_2ZrCl_2 decreased and that of the polyethylene produced by $TiCl_4$ increased with increasing amounts of TEA. In addition, it was also found that the molecular weight distribution of the polyethylene was broadened as the amount of TEA increased.

This indicated that the hybrid catalyst supported on the $SiO_2/MgCl_2$ bisupport is capable

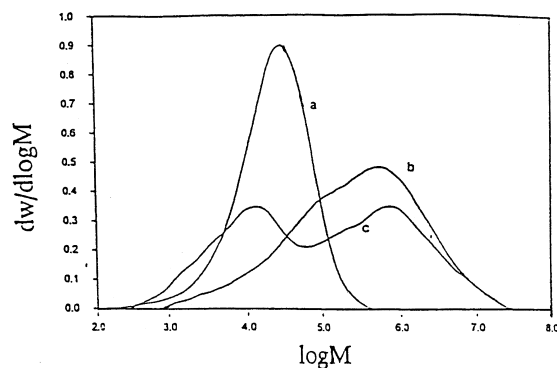Fig. 7. DSC results of polyethylene produced by Cp_2-$ZrCl_2/TiCl_4/TMA/SiO_2/MgCl_2$ catalyst: (a) Cp_2ZrCl_2 homo polymerization (MAO, Al/Zr = 1000); (b) TEA (Al/Ti = 100); (c) MAO (Al/Zr = 500) and TEA (Al/Ti = 100); (d) MAO (Al/Zr = 500) and TEA (Al/Ti = 57); (e) MAO (Al/Zr = 500) and TEA (Al/Ti = 29).

Fig. 8. Molecular weight distributions of the polyethylene produced by $Cp_2ZrCl_2/TiCl_4/TMA/SiO_2/MgCl_2$ catalyst: (a) Cp_2ZrCl_2 homo polymerization (MAO, Al/Zr = 1000); (b) TEA (Al/Ti = 100); (c) MAO (Al/Zr = 500) and TEA (Al/Ti = 100).
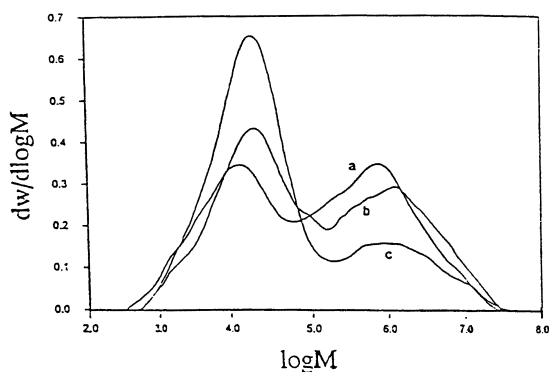
Fig. 9. Molecular weight distributions of the polyethylene produced by Cp_2ZrCl_2 /$TiCl_4$ /TMA/SiO_2 /$MgCl_2$ catalyst: (a) MAO (Al/Zr = 500) and TEA (Al/Ti = 100); (b) MAO (Al/Zr = 500) and TEA (Al/Ti = 57); (c) MAO (Al/Zr = 500) and TEA (Al/Ti = 29).

of producing a blend of polyethylenes, and that there is no strong chemical interaction between the two catalysts.

3. Conclusions

An $MgCl_2$/SiO_2 bisupport was prepared by agglomerating colloidal phase SiO_2 with an $MgCl_2$ solution. Magnesium was reasonably well distributed on both the surface and in the bulk of the bisupport. In terms of the treatment of prepared bisupports, TMA was superior to MAO with respect to the stability of the supported metallocene. The data clearly shows that the hybrid catalysts appear to be compatible on the $MgCl_2$/SiO_2 bisupport and, as a result, the produced polyethylene showed two different melting points and a bimodal molecular weight distribution pattern, corresponding to products arising from each catalyst.

4. Experimental

4.1. Materials

N_2 and ethylene (Sinyang Gas Products) of high purity were further purified before use by sequentially passing them through columns of a molecular sieve (Kokusan Chem.), anhydrous

P_2O_5 (Yakuri Chem.), and an oxygen scavenger (RIDOX, Fischer scientific). The molecular sieves were regenerated at 2-month intervals by treatment with a N_2 stream at 250 and the oxygen scavenger was activated by H_2 treatment at 250. Toluene (Oriental Chem.) was used as solvent for the catalyst preparation and was purified by distillation over Na metal to remove the trace of residual moisture. $MgCl_2$ (Aldrich Chem.), colloidal SiO_2 (LUDOX HS-40, DuPont), H_2SO_4 (Aldrich Chem.), Cp_2ZrCl_2 (Strem Chem.), $TiCl_4$ (Aldrich Chem.), TEA (Aldrich Chem.), MAO (type 4, Akzo Chem.) were used without further purification.

4.2. Support preparation

Three grams of anhydrous $MgCl_2$ was introduced into a glass reactor equipped with a magnetic stirrer and 10 ml of distilled water was then added. The mixture was heated to 50°C and stirred until the $MgCl_2$ was completely dissolved. Dilute H_2SO_4 (0.1 M) was then added dropwisely to the $MgCl_2$ solution at the room temperature to adjust the pH to 6.4. A 2.5 l amount of corn oil was introduced into a 4 l of cylindrical reactor. It was then stirred at a constant rate of 2000 r.p.m. Forty milliliters of colloidal SiO_2 was then rapidly introduced so that it was uniformly dispersed in the corn oil. Eight milliliters of $MgCl_2$ solution was then rapidly added and stirred 5 min. The agglomerated particles were separated, washed with *n*-heptane, and oven dried at 80°C for 8 h.

4.3. Catalyst preparation

4.3.1. Cp_2ZrCl_2 / TMA / MAO / SiO_2 / $MgCl_2$ catalyst

Fifty milliliters of toluene was introduced under a stream of N_2 into a glass reactor equipped with a magnetic stirrer and then 4 g of bisupport (SiO_2/$MgCl_2$) was suspended in it. Forty milliliters of 2 mol TMA (or MAO) solution was added dropwisely at 0°C and the mixture was allowed to react at 0°C for 2 h. This

reaction mixture was then washed five times with 100 ml of toluene at 80°C. The washed supports were suspended in 50 ml of toluene and reacted with 0.1 g Cp_2ZrCl_2 at 50°C for 2 h and then washed in the same way.

4.3.2. $TiCl_4 / TMA / SiO_2 / MgCl_2$ catalyst

Twenty milliliters of $TiCl_4$ was used in place of Cp_2ZrCl_2 in the $TMA/SiO_2/MgCl_2$ support. The support was reacted with $TiCl_4$ at 80°C for 2 h and then washed five times with 100 ml of toluene at 80°C.

4.3.3. $Cp_2ZrCl_2 / TiCl_4 / TMA / SiO_2 / MgCl_2$ catalyst

One gram of $TiCl_4/TMA/SiO_2/MgCl_2$ catalyst was suspended in 50 ml of toluene and reacted with 0.025 g Cp_2ZrCl_2 at 50°C for 2 h and then washed five times with 100 ml of toluene at 80°C.

4.4. Characterization

The morphology of the support was observed with scanning electron microscopy (SEM, JSM-840A, JEOL). The elemental contents on the surface of support were measured by SEM–EDS (JSM-840A, JEOL). The surface area of the catalysts was determined with a N_2-BET analyzer (ASAP-2000, Micromeritics). The contents of titanium, zirconium and magnesium in the catalyst were determined by ICP (VG PQ2-Turbo from VG elemental). The 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 molecular weight and molecular weight distribution of polyethylene were determined by the gel permeation chromatography (PL-210, Polymer Laboratory) at 160°C with trichlorobenzene as a solvent.

4.5. Polymerization of ethylene

Ethylene was polymerized in a 1 l glass reactor equipped with a magnetic stirrer under a constant ethylene pressure of 1.3 bar, using MAO and/or TEA as a cocatalyst. Three hundred milliliters of toluene and cocatalyst were introduced into the reactor under a stream of dry N_2 and then evacuated to remove N_2. Ethylene was then fed at a constant pressure. When required, hydrogen was fed prior to the ethylene supply. In this case, at first, hydrogen was fed at a pressure of 0.2 bar, and then ethylene was fed at a constant pressure of 1.3 bar including hydrogen. Polymerization was initiated by introducing the catalyst suspension into the reactor with a syringe. After a 50 min reaction time, the polymer was washed and dried in vacuum. The polymerization rate was determined from the amount of consumed ethylene, measured using a mass flowmeter.

Acknowledgements

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