Effect of Internal Lewis Bases on Recrystallized MgCl₂–TiCl₄ Catalysts for Polypropylene

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Synopsis

The effect of different Lewis bases in TiCl₄ catalysts supported on MgCl₂, which was modified by the recrystallization method, has been investigated in terms of activity, selectivity, and morphology. Ethyl benzoate (EB) and 2,2,6,6-tetramethylpiperidine (TMPip) were tested as the internal Lewis bases. Propylene polymerizations were performed at 50°C and 7 atm, using Al(C₂H₅)₃ as co-catalyst and TMPip as external modifier. Both supports and catalysts were characterized by BET, X-ray, SEM, and other techniques. It was found that the electron donor plays an important role in the recrystallization step of MgCl₂ from alcoholic MgCl₂ solution. Ethyl benzoate was the more effective internal donor leading to the porous, free-flowing, and stable high-activity catalyst, while TMPip was not so effective as internal donor owing to its decomposition by SiCl₄ during the support preparation. From short time polymerization kinetics, EB was found to increase both the values of the active site concentration ($[C^*]$) and the propagation rate constant (k_p). Comparison with the ball-milled catalyst has been made in view of the morphology. The morphology of the polymers formed with the recrystallized catalysts was the globule-like structure, while that with the milled catalyst was the broken structure due to its low surface area.

INTRODUCTION

There are numerous routines for preparing highly active supported catalysts for olefin polymerization.[1] These catalysts can be divided into the following three classes depending on their composition and method of support modification: (i) milling—milled product of TiCl₄ with MgCl₂ or magnesium powder in the presence of Lewis bases; (ii) precipitation—precipitation of highly disordered MgCl₂ from the dissolved MgCl₂ solution; and (iii) chemical conversion—reaction products of TiCl₄, alkylmagnesium, and electron donor compounds.

The well-known milling method has already been employed in commercial production. However, there still exists a limit to the control of the texture of the catalyst by the simple milling method. Accordingly much interest has been given to the precipitation and/or the chemical conversion methods to better control the catalyst texture. No matter what type of Mg compound (either MgCl₂·ROH or Mg compound solubilized in a medium and then precipitated out again, or MgR₂, Mg(OR)₂, etc.,) is used, MgCl₂ matrix will be ultimately re-formed.

In the precipitation method, the solubilization of MgCl₂ in the various media, the recrystallization of MgCl₂ from solution, and the possible synergistic effect

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between the electron donors are not clearly understood yet.[2] Since the electron donors (ED) play an important role in the recrystallization step of $MgCl_2$ from solution, they may affect the texture and activity of catalyst, the isotacticity of polymer, and the kinetic behaviors. In this work, two different Lewis bases, ethyl benzoate (EB) and 2,2,6,6-tetramethylpiperidine (TMPip) were tested as the internal electron donors in the $MgCl_2/ED/TiCl_4-Al(C_2H_5)_3$ system, in which the support $MgCl_2$ has been treated by precipitation method. Their effects on the catalyst performances were investigated. Comparison with the ball-milled catalyst has been made in view of the morphology of catalyst and polymer.

EXPERIMENTAL

Catalyst Preparation

For the catalyst preparation,[3] 4.76 g of anhydrous $MgCl_2$ was dissolved in a solution of 23.6 mL of 2-ethyl-1-hexanol (2E1H), 30 mL of n-decane, and the prescribed amount (ED/Mg mole ratio = 0.33) of Lewis base at 130°C, and then precipitated out with 50 mL of $SiCl_4$ in n-hexane. Ethyl benzoate (EB) and 2,2,6,6-tetramethylpiperidine (TMPip) were tested as internal Lewis bases. The resulting solid support was activated with 50 mL of $TiCl_4$ for 2 h at 80°C. After removal of excess $TiCl_4$ through a sintered glass funnel, the catalyst was washed with n-hexane (4–5 times at 50–60°C) and dried under vacuum at 20°C. The supports and catalysts are to be denoted by HS, HSP, or HSE, depending on the internal Lewis base. HS was prepared without any internal Lewis base, HSP with TMPip, and HSE with EB. Also a ball-milled catalyst with EB denoted by BME was prepared for comparison; 4.76 g of anhydrous $MgCl_2$ were ground with 2.36 mL of EB in a Fritsch Pulverisette ball mill (capacity: 45 mL; with five balls of 1.5 cm diameter and three balls of 1.2 cm diameter) at room temperature for 2 h, and activation with $TiCl_4$ was made as previously mentioned.

Polymerization

Polymerization was carried out in a 600-mL autoclave with 200 mL n-hexane under the following conditions: Ti = 0.5×10^{-3} g, Al/Ti = 50 mole ratio, propylene pressure = 7 atm, temperature = 50°C, and polymerization time = 1 h. $Al(C_2H_5)_3$ was used as co-catalyst and TMPip as external modifier. Polymer isotacticity was defined as the fraction insoluble in boiling n-heptane. The intrinsic viscosity was measured under nitrogen at 135°C in decalin, containing 0.1 wt % of 2,6-di-*tert*-butyl-*p*-cresol. The molecular weight was calculated by[4]

$$[\eta] = 0.917 \times 10^{-4} \, \bar{M}_n^{0.80}$$

Characterization

The titanium content in the catalysts was determined colorimetrically, and the content of Lewis base and 2E1H in the solid sample was measured by gas chromatography (GC). The surface area of supports and catalysts was measured by nitrogen adsorption technique at 78 K, on Area Meter II (Ströhlein Instruments). Samples of supports and catalysts were investigated with X-ray dif-

fractometer (Rigaku CN-2155D2) in order to analyze the structural change of modified $MgCl_2$.

RESULTS AND DISCUSSION

Electron Donor Analysis and Surface Area

Table I shows the data of the electron donor analysis and BET surface area. 2E1H was used to dissolve the anhydrous $MgCl_2$, which still remained in the precipitated supports. It indicates that 2E1H was not completely reacted with the recrystallizing agent, $SiCl_4$. But it was completely removed by the reaction with $TiCl_4$. EB remained in the supports HSE and BME, while TMPip was not detected in the support HSP. TMPip may have been decomposed by the recrystallizing agent $SiCl_4$. Therefore, it is believed that TMPip is not effective as an internal electron donor. The catalyst HSP produced with TMPip is expected to be close to the catalyst HS prepared without any Lewis base in view of the catalyst structure. Xiao et al.[5] indicated that EB contents of the supported catalyst prepared by the milling–soaking method were frequently higher than stoichiometric amounts of the $TiCl_4$–EB (1 : 1) complex. In the present study, similar results were obtained for the catalyst BME and also for the catalyst HSE prepared by the precipitation method.

The support HSE had a higher surface area than the other precipitated or milled supports (HS, HSP, or BME). It was observed that the support HSE was more uniform and free-flowing than the catalyst HS and HSP. Recrystallization leads to $MgCl_2$ particles composed of microcrystallites. The role of electron donor, by remaining in the microcrystalline interstices, seems to prevent their aggregation and lead to the formation of the pores among them, which resulted in the high surface area of the support. In this regard, the catalyst HSE is expected to be the most active, as to be shown in Table II later on. The second step of the catalyst preparation involved the treatment of precipitated product with excess $TiCl_4$. It is shown in Table I that the treatment of precipitated support with $TiCl_4$ resulted in the removal of most of 2E1H and a part of the EB. The precipitated supports showed drastic increase in the specific surface area with $TiCl_4$ treatment. The precipitated catalyst HSE is characterized by a lower content of EB and higher surface area than the milled catalyst BME. EB in the support HSE is more easily available for extraction with $TiCl_4$ due to larger surface area than the support BME. It is believed that the removal

TABLE I
Electron Donor Analysis and BET Surface Area

Sup.	2E1H (wt %)	ED (wt %)	BET area (m^2/g)	Cat.	Ti (wt %)	2E1H (wt %)	ED (wt %)	BET area (m^2/g)
HS	26.2	—	13	HS	4.0	0	—	91
HSP	22.3	0	24	HSP	7.4	0	0	43
HSE	10.5	28.0	81	HSE	1.7	0	18.0	151
BME	—	34.2	6	BME	4.4	—	27.1	9

of both 2E1H and EB at this stage considerably increased the specific surface area of the catalysts in the case of precipitated supports. The milled support BME showed little increase in surface area because 2E1H was not introduced in BME and also because less amount of EB was removed.

Catalyst Activity and Polymer Isotacticity

Table II shows the effect of Lewis bases on the activity of catalysts, both precipitated and ball-milled, and on the isotacticity and the molecular weight of isotactic polypropylene. The precipitated catalyst HSE with EB exhibited higher activity than any of the precipitated catalyst HS without any Lewis base, HSP with TMPip, and the milled catalyst BME with EB. The polymers obtained with the catalysts HS and HSP had higher $\bar{M}_n$ than those with the catalysts prepared with EB. Table II shows that TMPip used as external Lewis base increased the $\bar{M}_n$ of the isotactic polypropylene. Also, Chien et al.[5] obtained similar results for the ball-milled catalysts, that is, that the stereoregular polymers formed in the presence of external Lewis base had higher $\bar{M}_n$ than those obtained without it and that the internal Lewis base has the opposite effect on $\bar{M}_n$.

It should be noted here that the catalyst HSP shows a lower isotacticity (ca. 65%) than the catalyst HS without any Lewis base. It may be expected that the catalyst with more bulky electron donor, for example, HSP with TMPip in the present study, would result in the increase of isotacticity but the decrease of activity. However, the catalyst HSP resulted in the decrease of both activity and selectivity. Similar results were also obtained by Xiao et al.[6] with the milled catalysts, including piperidine or pyrrolidine as an internal donor. Therefore, the ineffectiveness of TMPip as internal electron donor seems to be due to its decomposition by $SiCl_4$ in the preparation step of the support HSP, as indicated in Table I. However, the use of TMPip as external Lewis base resulted in the increase of the isotacticity with only minimal loss of activity. The effectiveness of TMPip as external Lewis base can be attributed to its sufficient steric hindrance, which is presumed to prevent the complex formation at single vacancy isospecific sites but favors the complex formation at divacant nonspecific sites.[7]

TABLE II
Performances of Different Catalysts for Propylene Polymerization[a]

Cat.	Ti-content (wt %)	No ext. LB			TMPip/Al = 0.05		
		Activity[b]	I.I. (wt %)	$\bar{M}_n \times 10^{-5}$	Activity[b]	I.I. (wt %)	$\bar{M}_n \times 10^{-5}$
HS	4.0	4.7 (188)	71.4	7.8	4.0 (160)	85.0	9.0
HSP	7.4	1.5 (111)	64.8	7.4	1.2 (89)	89.3	8.8
HSE	1.7	13.7 (233)	76.0	4.5	9.5 (162)	92.0	6.0
BME	4.4	4.1 (180)	74.0	5.1	2.8 (123)	92.1	6.4

[a] 50°C, 7 atm Pc_3, Ti = 0.5×10^{-3} g Ti, Al/Ti = 50, 200 mL n-hexane, 1 h.
[b] Activity = kg PP/g Ti·h·atm(g PP/g cat·h·atm).

TABLE III
Kinetic Parameters of Propylene Polymerization[a] with Different Catalysts ([M] = 0.33 mol/L)

Catalyst	Fraction	I.I. (wt %)	Polymn. rate (mol/mol-Ti s)[b]	[C*] (mol %)	k_p (L/mol s)
HS	Overall		6.2	3.9	482
	Iso	60–79	4.7	2.3	619
	Ata		1.5	1.6	284
HSP	Overall		1.4	1.8	202
	Iso	70–73	1.0	1.0	242
	Ata		0.4	0.8	151
HSE	Overall		12.8	7.2	538
	Iso	75–84	10.4	4.3	732
	Ata		2.4	2.9	251
BME	Overall		3.3	3.0	333
	Iso	77–82	2.7	2.1	390
	Ata		0.6	0.9	202

[a] 50°C, 0.78 atm Pc$_3$, Ti = 0.5 mmol/L, Al/Ti = 50, 200 mL n-hexane.
[b] Mole of propylene/mole of titanium sec.

Kinetic–Molecular Weight Method

The four catalysts showed considerable change in activity with polymerization time, which is typical for Ziegler–Natta polymerization. However, these catalyst systems were found to have constant activity during the first short period (e.g., 1 min) from the start of polymerization in our experiment. In this short period, the active site concentration ($[C^*]$) and the propagation rate constant (k_p) of these catalyst systems can be assumed to be constant. The kinetic–molecular weight method[8,9] was used for determining $[C^*]$ and k_p from the following equation, expressing the relationship between the number of polymer chains $[N]$ and the polymer yield Y:

$$[N] = [C^*] + (k_{tr}[C^*]/R_p) \cdot Y$$

where R_p is the polymerization rate, k_{tr} the chain transfer rate constant, and $[N]$ obtained from Y and the average molecular weight number, $\bar{M}_n$, i.e., $Y/\bar{M}_n$. The concentrations of the isotactic, atactic, or overall active centers, $[C^*]_{iso}$, $[C^*]_{ata}$, or $[C^*]_{overall}$, were determined from the intercepts of the $[N]$–Y plot. R_p can be expressed by

$$Y = R_p \cdot t$$

$$R_p = k_p \cdot [M] \cdot [C^*]$$

where $[M]$ is the propylene concentration in the solvent ($[M] = 0.33$ mol/L under the present experimental conditions) and t is the polymerization time. R_p was obtained from the slope of Y–t plot, and then k_p was determined. All kinetic parameters of the short time polymerization are listed in Table III. The higher activity of catalyst HSE over the other catalysts is not only due to its higher active site concentration ($[C^*]$) but to its higher propagation rate con-
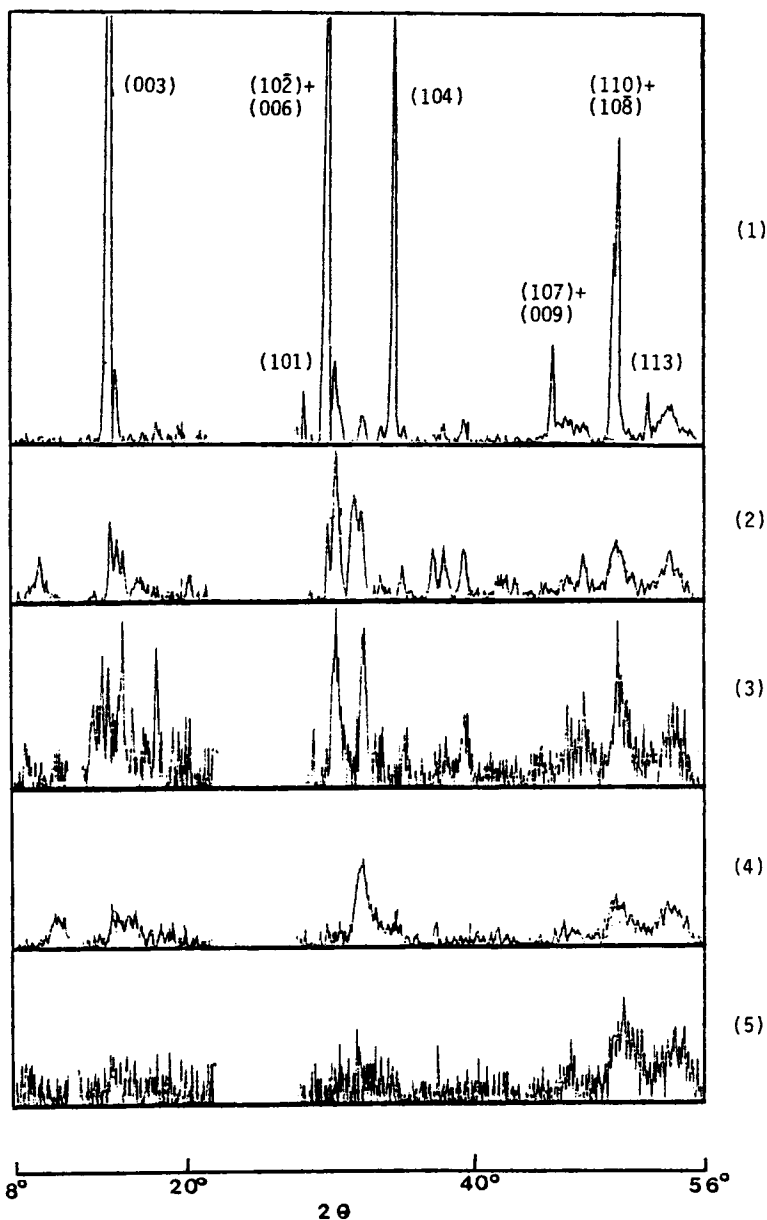
Fig. 1.   X-ray diffraction patterns of (1) $MgCl_2$, the supports; (2) HS; (3) HSP; (4) HSE; and (5) BME.

stant (k_p). The catalyst HSP showed the lowest values of both [C*] and k_p, which seems to be due to the decomposition of TMPip during the precipitation step.

X-ray Data

X-ray samples were prepared in a special hermetic curvette with a poly(ethyleneterephthalate) film window under inert atmosphere. Diffraction
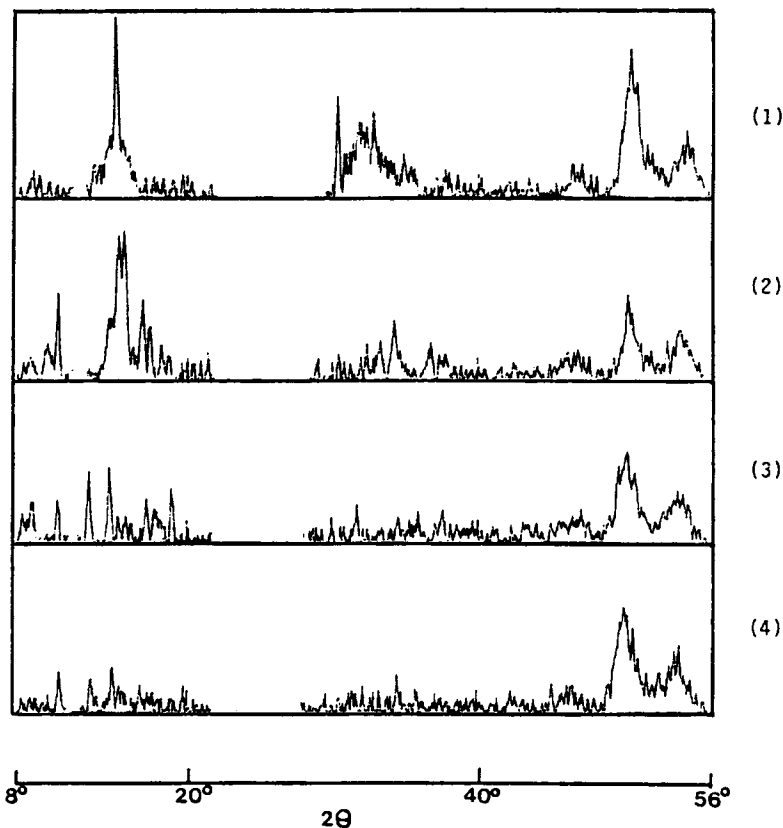
Fig. 2.   X-ray diffraction patterns of the catalysts (1) HS, (2) HSP, (3) HSE, and (4) BME.

pattern was taken in the range of $8° < 2\theta < 56°$. The diffraction peak at $21°$ of 2θ and the broad peak at $21–28°$ of the polymer film were omitted in Figures 1 and 2. Figure 1 shows that X-ray diffraction patterns of anhydrous $MgCl_2$ experienced considerable line broadening through precipitation or ball milling. The structure of $MgCl_2$ (from Aldrich Co.) seems to be similar to that of γ-$TiCl_3$ with cubic close-packed arrangement.[10] It was observed that ethyl benzoate accelerated line broadening of the $MgCl_2$ in the precipitation method. This phenomenon has been also observed in the milling process of $MgCl_2$ with ethyl benzoate.[11] Figure 2 shows the X-ray diffraction patterns after the treatment with $TiCl_4$. Upon treatment with $TiCl_4$ the diffraction peak at (110) direction recovered significantly. $TiCl_4$ is presumed to be inserted into the defect regions of $MgCl_2$ crystallites in the (110) plane, which resulted in some ordering of its structure. It should be noted that upon treatment of the support HSE and BME with $TiCl_4$, the crystallite size of $MgCl_2$ increases only in the (110) direction, and practically not at all in the (003) direction. For the catalysts HS and HSP, however, the treatment with $TiCl_4$ resulted in the increase of crystallite size in both the (110) and (003) directions. Note that the coordinatively unsaturated magnesium atoms are located in the crystal face of the (110) direction.
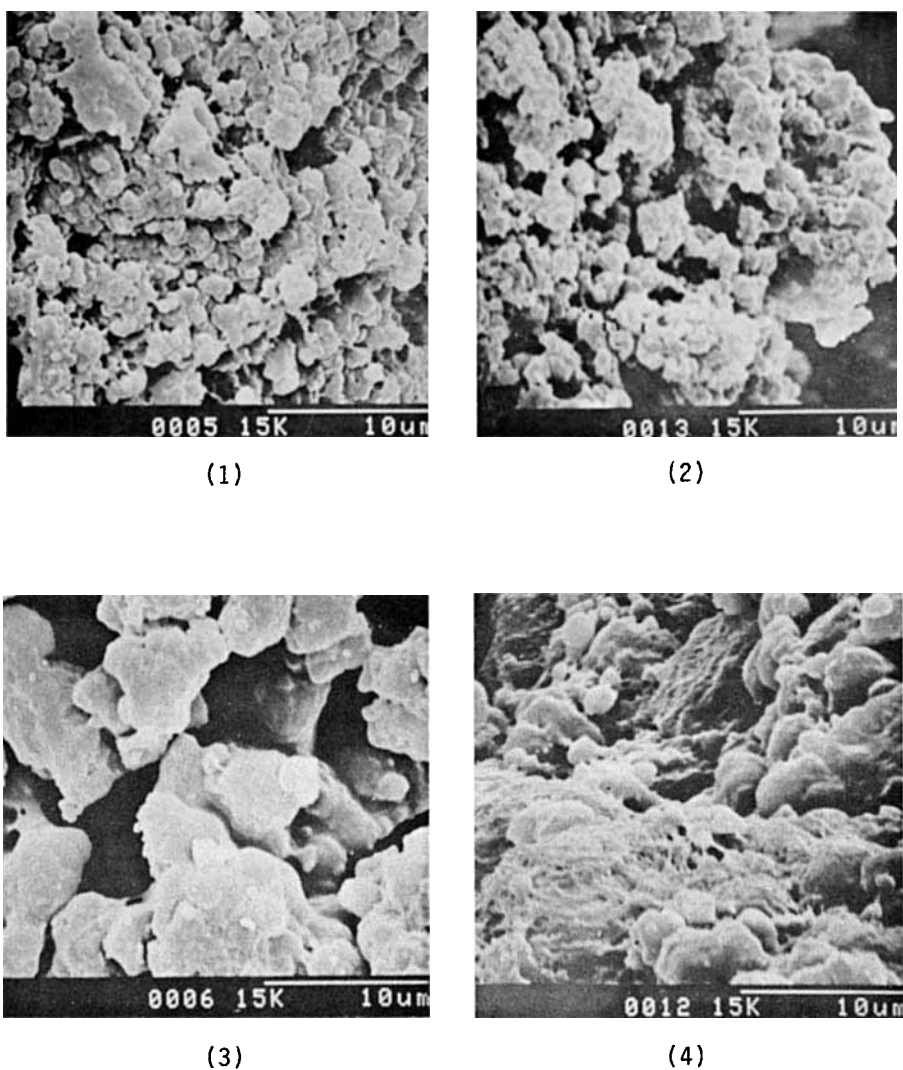
Fig. 3.   SEM photographs of polypropylene prepared with the catalysts (1) HS, (2) HSP, (3) HSE, and (4) BME under the same conditions at those in Table II ($\times$ 3000).

Polymer Morphology

Both activity and texture of the catalyst affect the polymer morphology. The polymerization catalysts are well known to replicate their morphology into the polymer particles. In other words, the catalyst particle acts as a template for growth of the polymer particle.[12] Figure 3 shows the morphology of the polymers produced. The morphology of the polymer produced with catalysts HS and HSP [Fig. 3(1) and 3(2)] is a small globule-like structure, which is known to be obtained from the polymer with unsupported catalyst TiCl$_4$. The morphology of the polymer particles with catalyst HSE [Fig. 3(2)] is a large globule-like structure with proper pore size. Figure 3(4) from the catalyst BME shows the

broken structure, which may be due to higher diffusion resistance of the polymer over the compact structure with low surface area. Among these, the morphology with HSE seems to have advantages in the increased plasticizing capability, better adsorption of stabilizers and dyes, due to the high surface area and porosity of the polymer granule.

CONCLUDING REMARKS

The effect of different Lewis bases in $TiCl_4$ catalysts supported on $MgCl_2$, which was modified by the recrystallization method, has been investigated in terms of activity, selectivity, and morphology. Ethyl benzoate was found to be a more effective electron donor than 2,2,6,6-tetramethylpiperidine, leading to the uniform, free-flowing, stable, and highly active catalyst. Short time polymerization kinetics indicated that ethyl benzoate increased both the values of the active site concentration ($[C^*]$) and the propagation rate constant (k_p). 2,2,6,6-tetramethylpiperidine was not effective as an internal electron donor possibly due to being decomposed by $SiCl_4$ in the preparation step. It was especially found that the electron donor (ED) plays an important role in the precipitation step of $MgCl_2$ from solution. The morphology of the polymers formed with the recrystallized catalysts was a globule-like structure, while that with the milled catalyst was the broken structure due to its low surface area.

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