

Effect of Diether as Internal Donor on MgCl₂-Supported Ziegler–Natta Catalyst for Propylene Polymerization

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ABSTRACT: This article demonstrates the influence of the molar ratio between diether as internal donor and Magnesium dichloride in processing of the catalyst preparation on the catalytic performance for propylene polymerization with MgCl₂-supported Ziegler–Natta catalyst. The effect of electron donor on catalyst is investigated. The experimental data find that diether content on catalyst increases and Ti content on catalyst decreases with the increase of diether/Mg molar ratio. This result indicates that diether as internal donor is not coordinated to Ti species but to Mg species on catalyst. The introduction of diether remarkably improves the cata-

lytic activity. The extents of improvement closely connect with diether/Mg molar ratio. The stereospecificity of catalyst intensively depends on the structure of diether as internal donor. The possible model of multi-active sites on heterogeneous Ziegler–Natta catalyst is proposed to explain these phenomena. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1399–1404, 2006

Key words: Ziegler–Natta catalyst; propylene polymerization; donor; stereospecificity; active sites model

INTRODUCTION

Ziegler–Natta (Z–N) catalyst has important effect on the development of polyolefin industry. Among the many factors that affect the performance of Z–N catalyst for isospecific propylene polymerization, electron donor (Lewis base) plays important role in ensuring the catalyst with satisfactory activity and stereospecificity.¹ In general, a complete Z–N catalyst system is required with both internal electron donor (added during catalyst preparation) and external electron donor (added during polymerization).² The most widely used electron donors are phthalate and alkoxysilane compounds as internal and external donors, respectively.³ With the discovery of 2,2-disubstituents-1,3-dimethoxypropane(1,3-diether),⁴ a novel and simplified generation of MgCl₂-supported catalysts had been developed. These diethers (used as internal donors) are known for having the property to produce highly active and stereospecific catalysts without any external donor.⁵ Some papers^{6–8} had investigated the effect of electron donor through contrasting the performance of Z–N catalysts containing different structure diethers; however, to the author's knowledge, there had been little reports studying the influ-

ence of the change of diether content on the performance of catalysts.

In this paper, two diethers are synthesized (shown in Fig. 1). One is 9,9-bis(methoxymethyl)fluorine (BMF), which had been already reported and could remarkably improve the stereospecificity of Z–N catalyst,⁵ and the other is 1,1-bis(methoxymethyl)cyclobutane (CBB), which is a novel donor devised.⁹ A series of catalysts is prepared through changing the molar ratio between donor and Magnesium dichloride in processing of the catalyst preparation. The performances of catalysts, which include the composition, polymerization activity, and stereospecificity, are investigated. The effects of electron donor are discussed. The possible model of multi-active sites on heterogeneous Z–N catalyst is used to explain the experimental results.

EXPERIMENTAL

Materials

Diethyl malonate and trimethylene chlorobromide were purchased from Aldrich. Propene (polymerization grade, from Yanshan Petrochemical Co.), TiCl₄ (from Beijing Yili Fine Chemical Co. Ltd) MgCl₂ (from Yingkou Science Chemical Co. Ltd.), and triethylaluminum (TEA, from Aybemarle Co., 95% purity) were used without further purification. Hexane and heptane were dried over molecular sieve (4 Å), then re-

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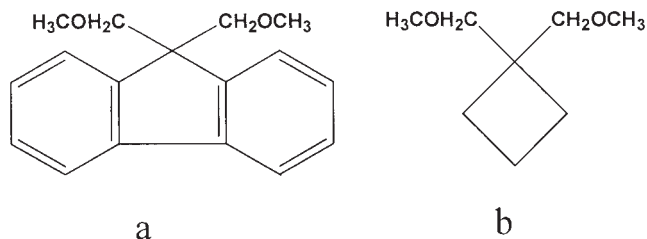


Figure 1 The structure of two internal electron donors: (a) 9,9-bis(methoxymethyl)fluorene (BMF) and (b) 1,1-bis(methoxymethyl)cyclobutane (CBB).

fluxed for 24 h over sodium, and distilled before use under nitrogen (extra pure grade, 99.99% purity). BMF and CBB were synthesized to methods described in the literatures.^{5,9}

Preparation of the catalyst

A Schlenk type reactor was used to prepare the catalysts. A large excess of TiCl₄ was introduced into the reactor and kept at -20°C. An amount of microspheroidal MgCl₂·2.5C₂H₅OH (strictly synthesized following our previous patent¹⁰) was added slowly, with agitation and maintained at this temperature for 30 min. The suitable internal electron donors (BMF or CBB) were/were not added after the temperature was raised to 60°C. The reactor mixture was allowed to react at 110°C for 2 h. The resulting solid was filtered and washed with hexane five times at 60°C and two times at room temperature. The final catalysts dried under vacuum were MgCl₂/TiCl₄, MgCl₂/TiCl₄/BMF, and MgCl₂/TiCl₄/CBB.

Polymerization

In a 250-mL reactor previously purged with nitrogen and propane, 100 mL anhydrous heptane was introduced into the reactor under propane flow. When no more propane was absorbed, suitable AlEt₃ as a cocatalyst and a prescribed amount of catalyst were respectively, added into the heptane solution in the reactor, and then the polymerization started. Propane pressure and temperature were kept constant during the reaction. After a period of time the polymerization was terminated by the addition of acidified ethanol. Polymer samples were precipitated with a large amount of ethanol, washed several times with ethanol, and then dried under vacuum at 60°C until the weight of the polymer was constant.

Characterization

The melting temperature (T_m) of the polymer was measured by means of differential scanning calorimeter (DSC), using a DSC-7 (Perkin-Elmer Co.) operat-

ing at a heating rate of 10°C/min from 50 to 200°C. T_m was determined in the second scan. Ti content was determined by spectrophotometer at 410 nm in the solution of catalyst, which was treated with sulfuric acid. Diether content was measured by gas chromatogram on heptane extract of the catalyst solutions. Isotacticity index of polypropylene was measured by IR method. The absorption ratio of A 974 cm⁻¹ (as an internal thickness measurement) to A 995 cm⁻¹ (indicative of the helical configuration) was directly related to the isospecificity.¹¹ Using an Ubbelodhe viscometer, we measured the intrinsic viscosity [η] of the polymer in decahydronaphthalene at (135 ± 0.1)°C and then the weight-average molecular weight (M_w) was calculated from the following equation.¹²

RESULTS AND DISCUSSION

Catalyst composition

Table I shows the influence of the Diether/Mg molar ratios in processing of the catalyst preparation on the catalyst composition. ZN0 does not contain any donor. BMF1–BMF6 contain BMF as internal donor and CBB1–CBB4 contain CBB as internal donor.

As shown in Table I, Ti content on ZN0 catalyst without any electron donor reaches the highest of 8.09%. With increasing Diether/Mg molar ratio during the preparation of catalyst, Ti content decreases and donor content increases. The changes of Ti and donor contents on catalysts containing BMF become further drastic in contrast with those on catalysts containing CBB. For example, Ti content on BMF3 catalyst drops to 4.91% from 8.09% and BMF content adds to 49.17% from 0 when the BMF/Mg molar ratio is 20/100; Ti content on CBB3 catalyst decreases to 6.40% from 8.09% and CBB content raises 16.11% when the CBB/Mg molar ratio is 20/100. The difference is due to the variety of donor structure. Comparing CBB with BMF (shown in Fig. 1), cyclobutane substitute group in CBB has a strong tension, weak electron-donating ability, and poor steric hindrance; however, fluorene ring in BMF has a proper bulkiness and strong electron-donating group, which links two methoxymethyl groups at C₉ (sp³ hybrid orbital).⁵ BMF is more strongly coordinated with Mg adjacent to active sites in comparison with CBB.

As usual, Infrared spectrum was used to investigate the reciprocity among compositions on catalyst.⁸ Figure 2 shows the FTIR spectra of Z–N catalyst and related compounds. The FTIR spectrum of BMF shows strong band of C–O stretching frequency at 1096 cm⁻¹ (curve a in Fig. 2). The C–O bands of TiCl₄/BMF (molar ratio 1 : 1) are shifted to a lower frequency at 1020 cm⁻¹ and 997 cm⁻¹ (curve b in Fig. 2). The bands at 1058 cm⁻¹ and 1035 cm⁻¹ manifest the presence of MgCl₂/BMF complex (curve c in Fig. 2). In fact

TABLE I
Effect of Diether/Mg Molar Ratio on the Composition of Catalysts

Catalyst	$MgCl_2 \cdot nC_2H_5OH$ (g)	Diether/Mg (10^{-2} mol/mol)	Catalyst	
			Ti (wt %) ^a	Diether (mmol %) ^b
ZN0	5	0	8.09	0
BMF1	5	10	6.22	29.8
BMF2	5	14	5.06	52.51
BMF3	5	20	4.91	49.17
BMF4	5	33	3.94	57.91
BMF5	5	50	3.57	60.67
BMF6	5	100	2.95	65.08
CBB1	5	5	7.30	7.29
CBB2	5	10	6.96	13.12
CBB3	5	20	6.40	16.11
CBB4	5	40	6.16	22.71

^a Ti contents (g Ti/100 g catalyst) were determined by spectrophotometer.

^b Diether contents (mmol diether/100 g catalyst) were measured by gas chromatogram.

IR C—O stretching frequencies for BMF3 catalyst (curve d in Fig. 2) are coincident with the frequencies for the $MgCl_2$ /BMF product and completely different from those of the $TiCl_4$ /BMF complex. This result indicates that BMF is not coordinated to Ti species but to Mg species on Z-N catalyst.

Figure 3 shows the Ti and donor contents on catalysts as function of the diether/Mg molar ratio. With BMF as the internal donor, the change of compositions on catalyst is shown in Figure 3(a). It is clear that the increase of BMF/Mg mole ratio during the catalyst preparation reduces Ti content and raises BMF content on catalyst. Obviously, there is a competitive balance between BMF and Ti on catalyst. The symmetrical change shows that diether excludes Ti and is not co-

ordinated to Ti on Z-N catalyst, consistent with FTIR result. With CBB as the internal electron donor, the change of compositions on catalyst is shown in Figure 3(b). It is evident that similar rule is observed. The increase of CBB/Mg molar ratio during the catalyst preparation decreases Ti content and raises CBB content on catalyst. Further observation in Figure 3(a) is that when BMF/Mg molar ratio is less than 20/100, Ti content rapidly falls and BMF content drastically rises; when BMF/Mg molar ratio is more than 20/100, the change of compositions on catalyst becomes smooth.

Active site model

It is well-known that active $MgCl_2$ crystalloid surface form defects and mono-nuclear or multi-nuclear Ti active sites contact with Mg through Cl bridge band.¹³ Because of the difference of binding energy, Z-N catalysts form multi-active sites. Recently, some models of multi-active sites had been proposed to explain experimental results. Busico et al.¹⁴ established three-site model based on high-resolution ^{13}C NMR data. Liu et al.¹⁵ proposed four types of active sites based on TREF analysis of produce. Kissin et al.¹⁶ considered that polymers produced with any heterogeneous Ti-based catalyst consist of at least four or five Folry components. In this paper, active sites are classified into two types (shown in Fig. 4). Type I represents poorly isospecific active site, in which a weak coordination with Mg exist. Furthermore, the unstable site could rapidly shift and rotate. The electron donor easily replaces Ti on the active site I, which inhabited the defects on $MgCl_2$ crystalloid surface; Type II represents highly isospecific active site. The stereospecificity and stability of the active site II may be significantly enhanced by donor, which coordinated to Mg ion adjacent to active species.¹⁷ It is a kinetic equilibrium between type I and type II on $MgCl_2$ -supported Z-N catalyst.

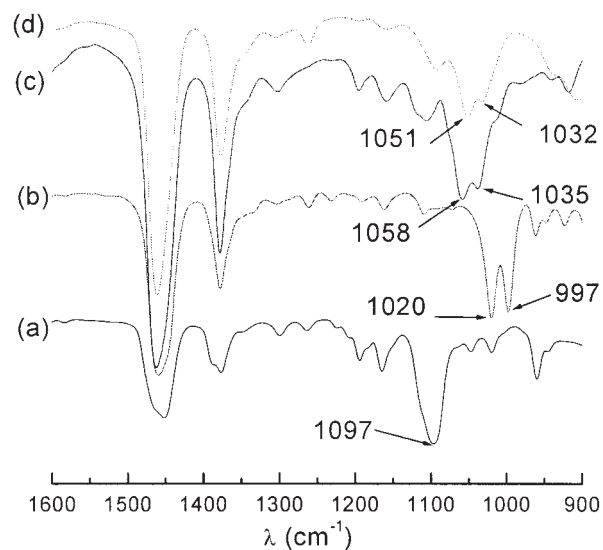


Figure 2 FTIR transmittance spectra of catalyst and related compounds: (a) BMF, (b) $TiCl_4$ /BMF complex (molar ratio 1:1), (c) $MgCl_2$ /BMF (comilled for 20 h), and (d) BMF3 catalyst (BMF/Mg = 1/5).

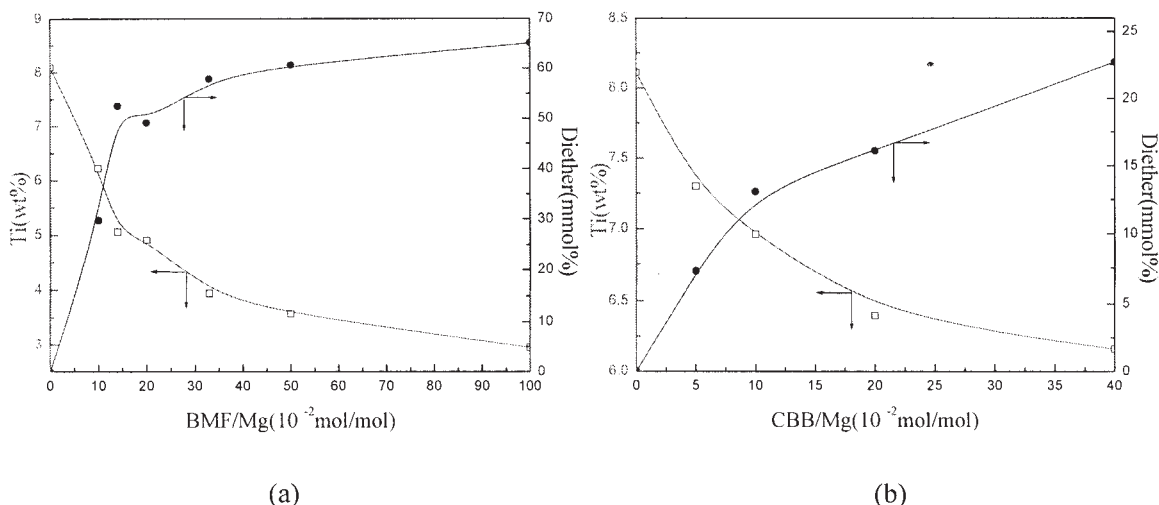


Figure 3 Effect of diether/Mg molar ratios during the catalyst preparation on Ti and diether contents: (a) Z-N catalyst containing BMF as internal electron donor and (b) Z-N catalyst containing CBB as internal electron donor.

When BMF/Mg molar ratio is less than 20/100, BMF, which is strongly connected with Mg on catalyst, can easily replace Ti on the unstable site I. The results show that Ti content on catalyst decreases rapidly and diether content increases greatly. Meanwhile, the proportion of active site I on catalyst fall. Along with further enhancement of BMF/Mg molar ratio, BMF has to compete with active site II on catalyst. Because of the good stability of active site II, BMF is difficult to replace Ti in the site. The change of compositions on catalysts becomes smooth.

Propylene polymerization

Table II shows the polymerization performance of Z-N catalyst as function of the diether/Mg molar ratio during the catalyst preparation. For $\text{MgCl}_2/\text{TiCl}_4$ catalyst, the activity of propylene polymerization is the lowest (No. 1). The addition of internal donor improves the catalytic activity. The extent of improvement is closely connected with diether/Mg molar ra-

tio. The stereospecificity of catalyst greatly depends on the structure of diether as internal donor.

The catalytic activity and isotacticity of polymer obtained as a function of diether/Mg molar ratio for propylene polymerization are shown in Figure 5. Obviously, with improving the diether/Mg molar ratio, the catalytic activity drastically increases. When diether/Mg molar ratio is a certain value, polymerization activity reaches the highest. At still higher diether/Mg molar ratio, a gradual decrease in the catalytic activity could be observed. For $\text{MgCl}_2/\text{TiCl}_4/\text{BMF}$ catalyst in Figure 5(a), the activity is the highest at BMF/Mg molar ratio of 20/100; for $\text{MgCl}_2/\text{TiCl}_4/\text{CBB}$ catalyst in Figure 5(b), the activity arrives to the highest at CBB/Mg molar ratio of 10/100.

As previously mentioned, without any electron donor, it is the balance state between active site I and active site II where Ti content on catalyst is the highest. The introduction of diether excludes part of the unstable active site I. The new defects are produced on MgCl_2 crystalloid surface. Donor inhabits one part of the defects and the other defects reform the stable active site II. It forms a new equilibrium among active site I, active site II, and electron donor. Ti content on catalyst and the sum of active sites reduce, however, the number of active site II increase. So, the addition of Lewis base improves the activity of propylene polymerization. When diether/Mg molar ratio increases to a certain value, the number of active site II and the catalytic activity together arrive to the highest point. Still increasing diether/Mg molar ratio, the stable active site II is also replaced by donor. Because of the decrease of the number of active site II, the catalytic activity reduces.

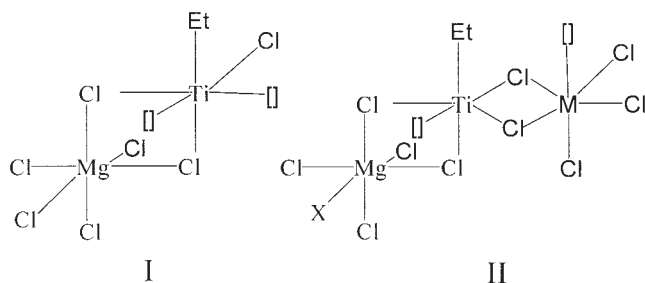


Figure 4 The possible model of active sites for poorly isotactic active site (I) and highly isotactic active site (II) on heterogeneous Ziegler-Natta catalysts.

TABLE II
Influence of Diether/Mg Molar Ratio on Propylene Polymerization^a

No.	Catalyst	Diether/Mg (10^{-2} mol/mol)	Activity (10^3 g PP/g Ti h)	I.I. (%) ^b	M_w (10^4)	T_m ^c (°C)
1	ZN0	0	2.77	75.0	16.3	157.9
2	BMF1	10	7.21	86.8	13.4	160.9
3	BMF2	14	7.57	92.5	14.6	162.6
4	BMF3	20	8.01	96.0	16.8	163.3
5	BMF4	33	7.64	93.6	15.8	163.8
6	BMF5	50	5.01	93.3	16.6	163.2
7	BMF6	100	3.80	92.3	16.3	162.7
8	CBB1	5	9.56	79.1	10.2	157.1
9	CBB2	10	11.0	74.0	11.6	157.4
10	CBB3	20	8.53	77.4	12.6	157.4
11	CBB4	40	4.35	75.2	10.6	157.9

^a Polymerization conditions: Catalyst, 50 ± 1 mg; heptane, 100 ml; propylene pressure, 0.1 MPa; cocatalyst, TEA; $n(Al)/n(Ti) = 40$; reaction temperature, 40°C; polymerization time, 30 min.

^b Isotacticity index was measured by IR.

^c Melting temperatures (second scan, at a heating rate of 10°C/min) determined by DSC.

The isotacticity of polymer obtained is intensively dependent on the stereospecificity of active sites. Therefore, it is possible that internal donor coordinated to $MgCl_2$ near active sites could improve the stereospecificity of the active Ti species.¹⁸

For Z-N catalyst containing BMF as internal donor in Figure 5(a), the stereospecificity of active site is closely connected with BMF/Mg molar ratio during the preparation of catalyst. Without any donor, the isospecificity of $MgCl_2/TiCl_4$ catalyst reaches the lowest of 75% (No. 1 in Table II). With increasing BMF/Mg molar ratio, the isotacticity of polymer rapidly improves. When BMF/Mg molar ratio is 20/100, the isotacticity arrives to the highest of 96% (No. 4 in Table II). At still higher molar ratio, a gradual decrease in the stereospecificity of catalyst could be observed.

On the basis of the previous model, the results could be explained. Because fluorine ring in BMF has a proper bulkiness and a strong electron-donating ability, which links two methoxymethyl groups at C_9 (sp^3 hybrid orbital), BMF coordinated to Mg ion neighboring Ti species drastically improves the stereospecificity of active site II. The introduction of BMF decreases the content of poorly isospecific active site I because of the instability of the sites. Meanwhile, the proportion of the stable and highly isospecific active site II on catalyst increases. The isotacticity of polymer rapidly improves. When BMF/Mg molar ratio is 20/100, the number of active species II is the highest. The isotacticity of catalyst reaches its maximum. At still higher BMF/Mg mole ratio, the stable active site II is gradually replaced by BMF. Ti content on catalyst reduces,

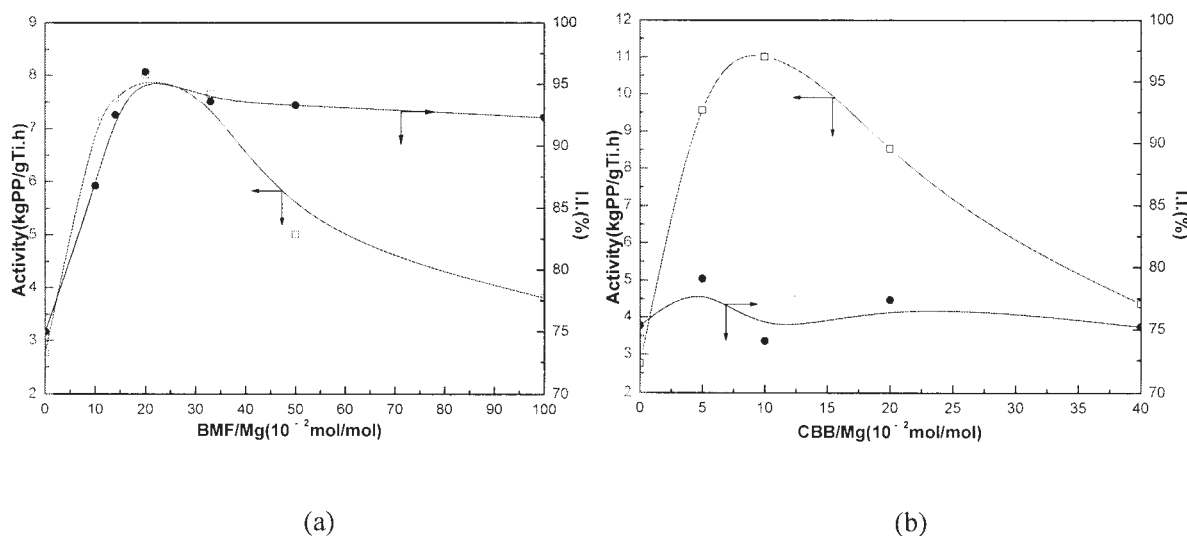


Figure 5 Influence of diether/Mg molar ratios during the catalyst preparation on the performance of propylene polymerization: (a) Z-N catalyst containing BMF as the internal donor and (b) Z-N catalyst containing CBB as the internal donor.

and the number of highly isospecific active site II falls, and so the stereospecificity of catalyst decreases slowly.

Comparing the isotacticity of $\text{MgCl}_2/\text{TiCl}_4/\text{CBB}$ catalyst with that of $\text{MgCl}_2/\text{TiCl}_4$ catalyst (No. 1, 8–11 in Table II), it is clear that the stereospecificity of catalyst does not change significantly as a function of CBB/Mg molar ratio in Figure 5(b). It is possible that the structure of electron donor plays an important role. Comparing CBB with BMF in Figure 1, cyclobutane in CBB has a strong tension, weak electron-donating ability, and poor steric hindrance; thus, CBB can hardly exert the effective influence to the stereospecificity of neighbor active sites. The isotacticity of polymer obtained is unsatisfactory.

CONCLUSIONS

In this work, we have investigated the effect of diether/Mg molar ratio in processing of the preparation of catalyst on the performance of MgCl_2 -supported Z–N catalyst. Two diethers (BMF and CBB) are used as the internal donors individually. Ti content on catalyst decreases with the increase of Diether/Mg molar ratio. Meanwhile, the change of diether content on catalyst presents the opposite trend. The symmetrical change shows that there is a competitive balance between donor and Ti on catalyst. Diether as internal donor is not coordinated to Ti species but to Mg species on catalyst.

The introduction of internal electron donor remarkably improves the catalytic activity. The extents of improvement closely connect with diether/Mg molar ratio. When diether/Mg molar ratio is a certain value, the highest catalytic activity appears. The stereospecificity of catalyst intensively depends on the structure of diether as internal donor. For $\text{MgCl}_2/\text{TiCl}_4/\text{BMF}$ catalyst, the increase of BMF/Mg molar ratio rapidly improves the stereospecificity of catalyst. When the ratio is 20/100, the isospecificity reaches the maxi-

mum. At still higher molar ratio, the isotacticity decreases slowly. For $\text{MgCl}_2/\text{TiCl}_4/\text{CBB}$ catalyst, the change of CBB/Mg molar ratio hardly influences the stereospecificity of catalyst. On the basis of the experimental results, the model of multi-active sites on heterogeneous Z–N catalyst that explains these observations is proposed.

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