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Study on the distribution of active centers in novel low Ti-loading $MgCl_2$-supported Ziegler-Natta catalyst*

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Abstract: Novel $MgCl_2$-supported Ziegler-Natta (Z-N) catalysts prepared using a new one-pot ball milling method can effectively control the amounts of Ti-loading in the catalysts. Complex GPC data on polypropylene synthesized by these novel catalysts were analyzed using the method of fitting the molecular weight distribution (MWD) curves with a multiple Flory-Schulz function. It was found that multiple active centers exist in these novel catalysts. Detailed study of the effects of the Ti-loadings in the catalysts on the distribution of the active centers showed that the Ti-loadings in the novel $MgCl_2$-supported Z-N catalysts might affect the proportion of each type of active centers; and might be the main factor responsible for the effect of the Ti-loadings on the microstructure, the molecular weight and molecular weight distribution width of the resultant polymer, the catalytic activity and polymerization kinetics.

Key words: Supported Ziegler-Natta catalyst, Propylene polymerization, Active center, Molecular weight distribution
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INTRODUCTION

Polypropylene is one of very important synthetic resins. In general, people pay more attentions to the development of catalysts with high isotactic specificity for propylene polymerization (Wang *et al.*, 1995; Soga and Shiono, 1997). However, with the development of the various use of polypropylene (Jiang and Wu, 1999; Tiemblo *et al.*, 1999), such as use of atactic polypropylene as an additive for building top grade highway recently, people began to make efforts to synthesize the catalyst for obtaining polypropylene with various kinds of novel microstructures. It was believed that the structures of the active centers in the catalysts and the way of growing the polymer chains have key effect on the microstructure of the polypropylene (Nele *et al.*, 2001; Bravakis *et al.*, 1998). It was proposed that low Ti-loadings in the catalysts may disperse Ti atom uniformly to form high proportion of a single Ti active center, producing highly non-stereospecific polypropylene, which has been confirmed using $MgCl_2$-supported $TiCl_3$ catalyst containing a small amount of Ti (about 0.1 wt%) (Shiono *et al.*, 1989). However, further research on the effect of the amount of Ti-loading on the dis-

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tribution of the active centers in the low Ti-loading Z-N catalyst and on the detailed polymerization characters of the low Ti-loading Z-N catalyst has not been reported yet.

This paper reports a novel one-pot ball milling method to prepare $MgCl_2$-supported and low Ti-loading Z-N catalysts which can synthesize novel non-stereospecific polypropylene; and also reports the results of study on the effect of the Ti-loadings in the catalysts on the types of active centers, their distributions and their polymerization characters by using the method of fitting the molecular weight distribution curve from GPC with a multiple Flory-Sclulz function.

MATERIALS AND METHODS

Materials

Anhydrous $MgCl_2$ was used as received. Hexane was refluxed over an Na-K alloy before use. $AlEt_3$ was obtained commercially and used without further purification. Petroleum ether was dried over 4A molecular sieves before use. Polymerization grade propylene was further purified by passing it over two columns of pre-activated molecular sieves 4A. Nitrogen of extra-pure grade, 99.99%, was dried by passing it over two columns of pre-activated molecular sieves 4A to remove residual moisture and oxygen.

Preparation of the supported catalyst

A novel one-pot ball milling method for preparing the catalysts was developed as depicted in Fig.1 simply. Its milling procedure is divided into three stages: grinding of single $MgCl_2$, grinding after pouring into $TiCl_4$ solution in hexane and grinding after removing hexane. This preparation procedure is not only simple and easily industrialized, but can also effectively control the amount of Ti-loadings in the catalysts and makes it possible disperse Ti atom uniformly to form a specifically active center mainly. All manipulation was carried out under dry, oxygen-free nitrogen.

Polymerization procedure and GPC analysis

Propylene polymerizations were carried out in a 100-ml, three-necked glass reactor equipped with a magnetic stirrer. Required amounts of petroleum ether, $AlEt_3$ and the catalyst were introduced in this order. Propylene was continuously supplied to keep pressure at 1 atm and the propylene consumption was detected by a monitoring system and recorded by a computer. The polymerizations were stopped after 1 h and the polymers were precipitated by the addition of acidified alcohol. The resultant polymer was filtered off, washed with alcohol and dried in vacuum to constant weight.

The molecular-weight distribution of the polypropylene sample was determined with a PL-220 GPC apparatus.

Fitting MWD with multiple Schulz-Flory most-probable distribution

Many researchers proved that there are multiple types of active centers in the supported Z-N catalyst (Doi *et al.*, 1981; Locatelli *et al.*, 1990); and that the MWD curve of the resultant polymer could be formed by adding together the MWD curve of the polymer produced by each type of active center. The mathematical expression is (Kissin, 1995):

$$W(\ln M) = \Sigma a_i b_i^2 M^2 \exp(-b_i M) \quad (1)$$

where $a_i b_i^2 M^2 \exp(-b_i M)$ is the mathematical expre-

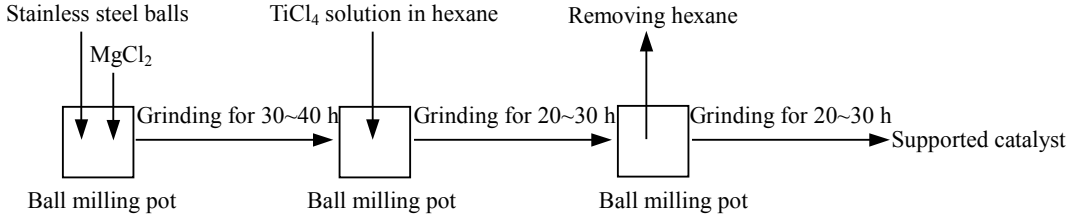

Fig.1 A novel one-pot ball milling preparation of the low Ti-loading $MgCl_2$-supported catalysts

ssion of the most probable distribution of the active center type i; a_i and b_i are two parameters determining the position and area of the peak in the GPC curve. And the generalized weight distribution function of ln$M$ of the active center type i is:

$$g_i(\ln M)=\frac{a_i b_i^2 M^2 \mathrm{e}^{-b_i M}}{\int_0^{+\infty} a_i b_i^2 M^2 \mathrm{e}^{-b_i M}\mathrm{d}(\ln M)} \tag{2}$$

We name the average molecular weight of the polymer produced by each type of active centers as $\overline{M}_1, \overline{M}_2, \overline{M}_3$ … respectively. From the definition of the weight average molecular weight, Eq.(3) can be obtained:

$$\overline{M}_i=\int_0^{+\infty} M g_i(\ln M)\mathrm{d}(\ln M) \tag{3}$$

From Eqs.(2) and (3), we can obtain the following expression:

$$\overline{M}_i=\int_0^{+\infty} M\times\frac{a_i b_i^2 M^2 \mathrm{e}^{-b_i M}}{\int_0^{+\infty} a_i b_i^2 M^2 \mathrm{e}^{-b_i M}\mathrm{d}(\ln M)}\mathrm{d}(\ln M)=\frac{2}{b_i} \tag{4}$$

In addition, we also name f_{A1}, f_{A2}, f_{A3}… respectively as the polymer weight percentage produced by each type of active center of the whole polymer. The mathematical expression is:

$$f_i=\frac{\int_0^{+\infty} a_i b_i^2 M^2 \mathrm{e}^{-b_i M}\mathrm{d}(\ln M)}{\sum_{i=1}^{6}\int_0^{+\infty} a_i b_i^2 M^2 \mathrm{e}^{-b_i M}\mathrm{d}(\ln M)}=\frac{a_i}{\sum_{i=1}^{6} a_i} \tag{5}$$

Each group of parameters a_i, b_i can be obtained by fitting MWD curves of the resultant poly-propylene synthesized by low Ti-loading $MgCl_2$-supported Z-N catalyst with a multiple Flory-Schulz function, so $\overline{M}_i$ and f_i can be calculated according to Eqs.(4) and (5).

RESULTS AND DISCUSSIONS

Effect of Ti-loading amount on the distribution of the active centers.

Molecular weight and molecular weight distribution of the polypropylene prepared with the novel $MgCl_2$-supported and low Ti-loading Ziegler-Natta catalyst are listed in Table 1 showing that the molecular weight distribution width of the polymer is wide and ranges from 3 to 8.

Table 1 Results of the propylene polymerization using catalyst with different Ti-loadings

[Al/Ti]	Ti-loadings (wt%)	Activity (kg P/g Ti·h)	M_w ($\times10^4$)	M_w/M_n
20	0.4	1.1	7.1	5.4
	0.8	2.6	7.2	5.4
	2.0	1.8	8.3	6.8
40	0.4	1.2	5.1	6.2
	0.8	3.5	5.2	6.2
	2.0	1.0	5.2	7.8
60	0.4	0.9	2.4	3.6
	0.8	2.2	2.8	3.8
	2.0	1.7	5.4	6.4

In general, the wide molecular weight distribution is mainly due to the diffusion procedure and multiple active centers in the catalysts. In our polymerization experiments, the resultant polymer was a highly non-stereospecific, which means the polypropylene had high solubility in petroleum ether. So we can consider that the factor of diffusion is limited and that the wide molecular weight distribution is mainly due to plurality of active centers in the catalysts (Xu *et al.*, 1998; Fan *et al.*, 1991).

The fitting results on the GPC data of the resultant polymer are shown in Table 2. It was found that these MWD curves were actually fitted with 6 Schulz-Florry most-probable distribution. Fig.2 shows some results fitting experimentally molecular weight distributions with the most-probable distribution.

Table 2 shows that the effect of the variation of Ti-loadings in the catalyst on M_i is little except at high Al/Ti ratio and low Ti-loadings. At Ti-loadings of 0.8% and 0.4%, each f_i had little change; but that when the Ti-loadings reached 2%, f_1+f_2 increased while f_3+f_4 decreased. These phenomena may be interpreted as follows: at the low Ti-

Table 2 Results of the fitting MWD curves of the polymer produced by different Ti-loading catalysts

Al/Ti	Ti %	M_1 ($\times10^{-4}$)	M_2 ($\times10^{-4}$)	M_3 ($\times10^{-4}$)	M_4 ($\times10^{-4}$)	M_5 ($\times10^{-4}$)	M_6 ($\times10^{-4}$)	f_1 (%)	f_2 (%)	f_3 (%)	f_4 (%)	f_5 (%)	f_6 (%)
20	0.4	32.5	11.2	4.6	1.8	0.5	0.2	6.9	20.1	38.4	25.7	7.1	1.8
20	0.8	34.5	11.9	4.6	1.8	0.5	0.2	7.1	20.3	38.1	25.5	7.3	1.7
20	2.0	32.2	10.9	4.5	1.8	0.6	0.2	9.9	21.4	32.9	26.4	8.2	1.2
40	0.4	38.7	11.8	4.4	1.7	0.6	0.2	3.9	11.8	30.9	32.6	13.6	7.2
40	0.8	40.5	12.5	4.4	1.7	0.6	0.2	4.1	13.1	31.7	32.5	13.5	5.1
40	2.0	38.1	11.7	4.4	1.8	0.6	0.2	4.0	16.3	34.2	28.9	12.6	4.0
60	0.4	–	7.8	3.6	1.7	0.5	0.2	–	5.2	34.5	40.5	14.6	5.2
60	0.8	27.1	8.1	3.7	1.7	0.5	0.2	1.5	5.4	34.2	39.8	14.1	5.0
60	2.0	35.5	11.8	4.4	1.8	0.6	0.2	4.5	13.9	33.7	31.1	12.4	4.5

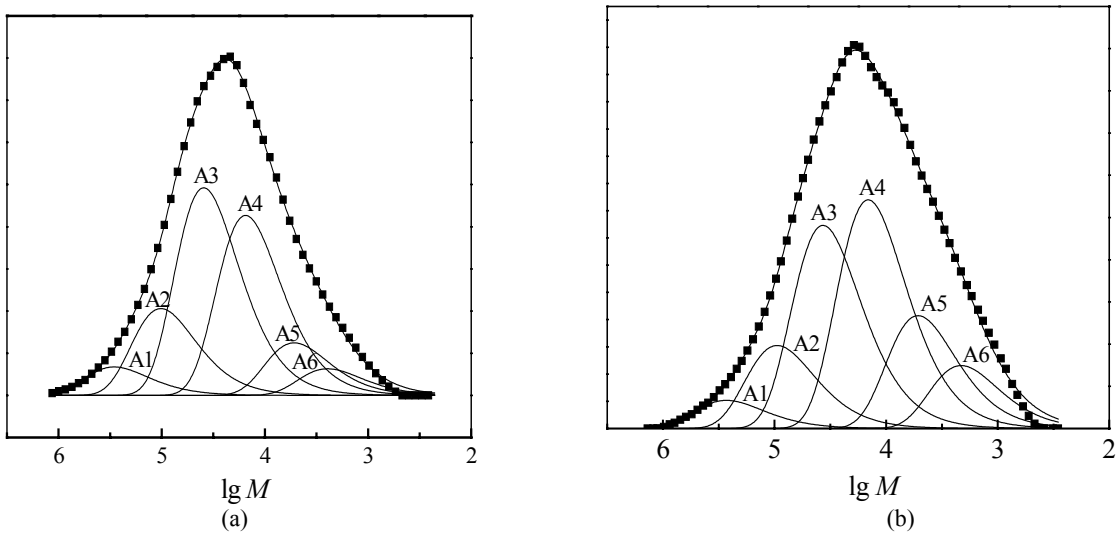

Fig.2 Fitting experimental molecular-weight distribution with most-probable distribution
(dots: experimental data; lines: six Flory-Schulz MWD functions and their sum)
(a) Al/Ti=40, Ti%=2.0%, T=50 °C; (b) Al/Ti=40, Ti%=0.4%, T=50 °C

loadings (0.4% and 0.8%), Ti atoms probably is in a single dispersion and the proportion of each type of active centers has little change, and so the proportion of the polymer produced by the each type of active centers also has little change; but at the high Ti-loadings (2.0%), part of Ti atoms will not be in the single dispersion, which may lead to the increase of the proportion of isotactic active centers producing the high molecular weight polymer.

Effect of Ti-loading amount on the molecular weight and molecular weight distribution width

From Table 1, it can be found that the molecular weight and molecular weight distribution of the resultant polymer produced by the catalysts with Ti-loadings of 0.8% and 0.4% is almost equal, but that when the Ti-loadings reaches 2%, both the molecular weight and molecular weight distribution width increase. The reason for this phenomena may be related to the proportion of the polymer produced by the each type of active center. Variation of Ti-loadings may give rise to the change of the proportion of each type of active center.

In general, as f_1+f_2 increases, the molecular weight increases; and as f_3+f_4 decreases, the molecular weight distribution width increases. From Table 1 and Table 2, we can find that the effect of Ti-loading amount on the calculated value of f_i is consistent with the effect of Ti-loading amount on the experimental data of the molecular weight and molecular weight distribution width of the resultant polymer.

Effect of Ti-loading amount on the catalytic activity and polymerization rate

From Table 1, we can find that the catalytic activity maximized at Ti-loadings of 0.8%. The possible reason was that at low Ti-loadings, almost all of the Ti atoms were in single dispersion; and that at the same impurity level, the lower the Ti-loadings in the catalyst, the higher the proportion of the deactive center, and so the catalytic activity of low Ti-loading catalyst decreased; and at high Ti-loadings, the decrease of catalytic activity was probably due to the increase of the proportion of not activated Ti atoms and isotactic active centers with low polymerization rate.

Fig.3 shows some polymerization-rate curves using Ziegler-Natta catalysts prepared with different Ti-loadings. It can be found that the polymerization rate is highest at Ti-loadings of 0.8%, and at the first 20 minute of the polymerization, the polymerization rate of the Ti-loadings of 0.4% is faster than that of the Ti-loadings of 2.0%, but after 20 minute of the polymerization, the reverse happens. The probable reason is that the proportion of the atactic active centers in the catalyst of the Ti-loadings of 0.4% is higher than that of the Ti-loadings of 2.0%; and that the deactivating rate of the active centers in the catalyst of the Ti-loadings of 0.4% is faster than that of the Ti-loadings of 2.0%.

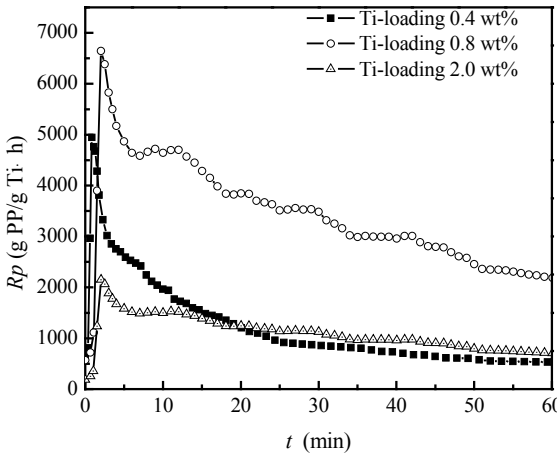

Fig.3 The effect of the Ti-loading amount on the polymerization rate

Polymerization condition: Al/Ti=40; *T*=40 °C; 1 atm; 1 h

CONCLUSION

A novel one-pot ball milling method to prepare Z-N catalyst was established. Using this novel method, we obtained the novel low Ti-loading $MgCl_2$-supported catalysts, which can produce polypropylene with a novel microstructure. Analyzing of GPC data on the resultant polymer revealed that multiple active centers exist in these novel catalysts; and that the effect of the amounts of Ti-loadings on the catalytic activity and polymerization rate was mainly due to the effect of the amounts of Ti-loadings on the proportion of each type of the active centers in the catalyst. For Ti-loadings lower than 0.8%, almost all of the Ti atoms are in a single dispersion; and the effect of the Ti-loadings on the proportion of each type of active centers is little, but for high Ti-loadings, the variation of the Ti-loadings causes change in the proportion of each type of active center.

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