

Molecular Weight Distribution of Polyethylene Catalyzed by Ziegler–Natta Catalyst Supported on MgCl₂ Doped with AlCl₃

Yong-Ping Chen,^{1,2} Zhi-Qiang Fan,¹ Jian-He Liao,² Shuang-Quan Liao²

¹The Institute of Polymer Science, Zhejiang University, Hangzhou 310027, China

²Department of Polymer Science and Engineering, South China University of Tropical Agriculture, Danzhou 571737, Hainan, China

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ABSTRACT: Ti-based Ziegler–Natta catalysts supported on MgCl₂ doped with AlCl₃ were prepared by the reaction of MgCl₂/AlCl₃–ethanol adduct with TiCl₄. No AlCl₃ crystallites were found in the AlCl₃-doped catalysts by WAXD analysis, suggesting that AlCl₃/MgCl₂ solid solution was formed. The effect of doping on the catalyst performance in ethylene polymerization was investigated. The results showed that the catalysts based on AlCl₃-doped MgCl₂ support exhibited a slightly higher activity than did the MgCl₂-supported catalyst and the molecular weight distribution (MWD) of polyethylene (PE) markedly increased

(from 10.8 to 47.9) with the increase of AlCl₃ content in catalysts. The changes in catalyst's active center distribution were studied based on nonlinear fitting of the polymer GPC curves by multiple Flory functions. It was found that increase of types of active centers by introducing AlCl₃ into the support should be responsible for the broadening of MWD of PE. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1768–1772, 2006

Key words: supported catalysts; AlCl₃; ethylene polymerization; Ziegler–Natta catalysis

INTRODUCTION

Polyethylene (PE) has the highest production volumes of all synthetic polymers, because of its many advantages, e.g., excellent chemical resistance, high impact strength, and stiffness even at low temperatures.¹ It is well known that molecular weight (MW) and molecular weight distribution (MWD) play a very important role in determining the physical and mechanical properties of polymers. High-MW PE has good mechanical properties, but it is difficult to process. An increase in MWD tends to improve the melt flow rate at high shear rate, which is important for blow molding and extrusion techniques.^{2,3} Therefore, it is necessary to control the MW and MWD of polyethylene to optimize both the physical and rheological properties. It has been recognized that polyethylene with broad or bimodal MWD can reach an excellent balance between mechanical and rheological properties.

Several methods for controlling MW and MWD are available, such as: physical blending of the polymers with different average MW, cascade reactor process,⁴ and using composite of different catalysts in a single-

reactor polymerization process. However, these methods more or less have some defects such as gelation, high cost, and complex manipulation, etc. Accordingly, it is necessary to seek a single catalyst system producing broad or bimodal MWD PE in a single reactor.⁵

It has been well known that heterogeneous Ziegler–Natta catalysts produce polymers with broad MWD, because of the presence of multiple active centers residing in the heterogeneous catalysts. The active centers differ from one another with respect to the average molecular weight of the polymers they produce, their kinetic behavior, and their stereospecificity. It is believed that the MWD and chain structure distribution of the polymer are mainly determined by the active center distribution (ACD) of the catalyst. It is widely accepted that a large percentage of active sites are formed at the edges, cuts, and surface defects of MgCl₂ crystallites. Doping MgCl₂ with inorganic salts can change the distribution of these defects and thus change the ACD of the catalyst. There are a few literatures reporting control of MWD of polymer through modification of MgCl₂-supported Ti-based catalyst by doping inorganic compounds in the support, such as MnCl₂,⁶ ZnCl₂,⁷ and NaCl.⁸

In the present work, we have prepared four MgCl₂/AlCl₃/TiCl₄ type supported catalysts with different AlCl₃ content, with the aim of investigating the influences of doped AlCl₃ on the MWD of PE produced by the catalysts. The changes in ACD were studied based on

Correspondence to: Z.-Q. Fan (fanzq@zju.edu.cn).

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deconvolution of the MWD curves by multiple Flory functions.

EXPERIMENTAL

Materials

All operations were performed under a dry argon atmosphere with standard Schlenk techniques. Ethylene, hydrogen, and argon were purified by passing through preactivated columns packed with molecular sieves and oxygen scavenger to remove residual traces of oxygen and moisture. *n*-Heptane was freshly distilled under refluxing in the presence of Na/benzophenone. Diphenyldimethoxysilane (DDS) used as external donor was distilled in vacuum and diluted to 0.2 mol/L solution in *n*-heptane. Triethylaluminum (TEA, Fluka, diluted into 1 mol/L solution in *n*-heptane), TiCl₄, anhydrous MgCl₂, and anhydrous AlCl₃ were used without further purification.

Preparation of support and catalyst

Calculated amounts of anhydrous MgCl₂, AlCl₃, and ethanol in a molar ratio ($n(\text{MgCl}_2 + \text{AlCl}_3) : n(\text{EtOH})$) of 1 : 3 were added into a glass reactor equipped with a magnetic stirrer, and equal volume of *n*-heptane was added. The mixture was heated to about 120°C and stirred until the MgCl₂ and AlCl₃ were completely dissolved. Adduct of (MgCl₂ + AlCl₃) with EtOH was slowly precipitated when the system was cooled to room temperature. Then the solvent and the remained ethanol were removed by evacuation. The dried adduct powder was sealed and stored in a glass bottle.

TiCl₄ (100 mL) was injected into a three-neck flask and cooled to below 0°C, and about 10 g adduct powder was introduced into the flask under stirring. The temperature was slowly raised to 120°C and maintained for 2 h and then lowered to 60°C. The supernatant liquid was siphoned off. A second batch of TiCl₄ (80 mL) was introduced into the flask and stirred at 120°C for 2 h. After the same cooling and separation operations as

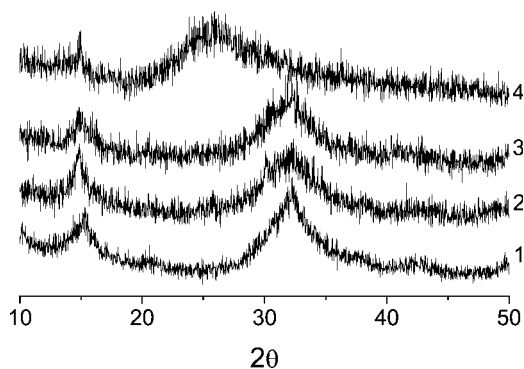


Figure 1 WAXD patterns of supported catalysts (1: Cat-A, 2: Cat-B 3: Cat-C, 4: Cat-D).

TABLE I
Ti, Mg, Al, and Cl Contents of the Catalysts

Catalysts	Cat-A	Cat-B	Cat-C	Cat-D
AlCl ₃ feed dosage ^a	0	14.5	28.7	100
Ti content ^b	8.2	9.6	8.4	1.5
Mg content ^b	17.1	12.6	11.0	0
Al content ^b	0	2.4	5.2	18.9
Cl content ^b	71.5	73.0	72.6	77.4

^a Weight percentage calculated from AlCl₃/(AlCl₃ + MgCl₂).

^b Weight percentage found in the catalysts.

before, the remained solid was washed five times each with 100 mL *n*-heptane. Then the catalyst was dried in vacuum and stored under argon.

Ethylene polymerization

Polymerization runs were carried out in a 100 mL Schlenk bottle at 60°C. The bottle was charged with 50 mL anhydrous *n*-heptane as reaction medium. Required amounts of cocatalyst (TEA), external donor (DDS), and the catalyst were introduced in sequence into the reactor and 25 mL hydrogen was injected into the reactor by a syringe. Ethylene was then fed into the reactor at a constant pressure of 1 atm during the polymerization. 30 min later, the polymerization was stopped by the addition of a dilute hydrochloride acid solution in ethanol. The polymer was filtered, washed with ethanol, and dried in vacuum.

Characterization

The Ti, Mg, and Al contents of the catalysts were measured using inductively coupled plasma (ICP; IRIS Intrepid IIXSP, Thermo Electron). The Cl content of catalysts was determined by ion chromatography using a Dionex ICS2000 spectrometer.

Wide-angle X-ray diffraction (WAXD) of the catalysts was performed in a Rigaku D/max-rA diffractometer with Cu K α target and 40 kV.

The molecular weight (MW) and molecular weight distribution (MWD) were measured by gel permeation chromatography (GPC, PL-220, Polymer Laboratories Ltd.) at 150°C with 1,2,4-trichlorobenzene as the solvent. Three PL-mixed B columns (50–10⁷) were used and universal calibration against narrow polystyrene standards was adopted.

RESULTS AND DISCUSSION

WAXD analysis of the catalysts

WAXD patterns of the catalysts are shown in Figure 1 and composition of the catalysts is listed in Table I. As shown in Figure 1, the profile of Cat-B and Cat-C is very

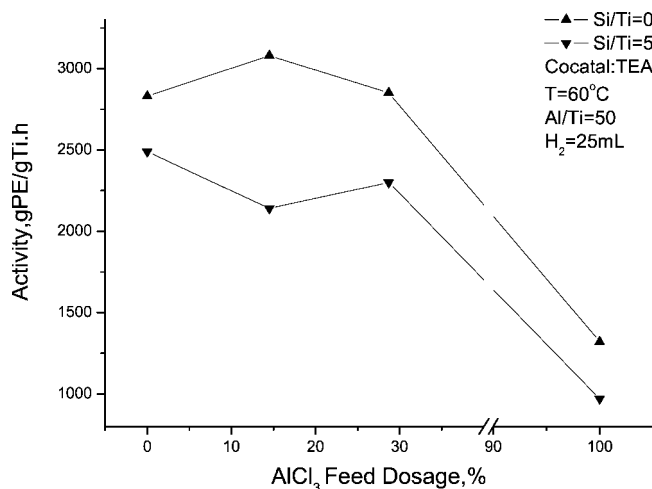


Figure 2 Activity of ethylene polymerization catalyzed by AlCl_3 -doped catalysts activated with TEA.

similar to that of Cat-A. A "halo" can be observed at $20 = 20\text{--}30^\circ$ in AlCl_3 -supported catalyst (Cat-D) but not to be seen in Cat-B and Cat-C, which also contain some AlCl_3 . It means that no crystallites of AlCl_3 can be found in these two catalysts. It can be deduced that AlCl_3 has been dissolved in MgCl_2 and an $\text{AlCl}_3/\text{MgCl}_2$ solid solution has formed.

Composition of the catalysts

The resulting content of Ti, Mg, Al, and Cl found in the catalysts are listed in Table I. It can be seen that the Ti content of the AlCl_3 -supported catalyst (Cat-D) is much lower than that of the other three catalysts, because MgCl_2 is the best support for the Ti catalysts,⁹ but AlCl_3 is not an effective support for anchoring TiCl_4 . Even so, Ti content of Cat-B and Cat-C, into which AlCl_3 was introduced, is slightly higher than that of the MgCl_2 -supported catalyst (Cat-A). In words of the Ti/Mg weight ratio, the values of the two $\text{MgCl}_2/\text{AlCl}_3/\text{TiCl}_4$ type catalysts (both 0.76) are much higher than Cat-A (0.48). This result may be explained by increase in the

TABLE II
Molecular Weight and MWD of PE Catalyzed by Different Catalysts^a

Run	Catalyst	Si/Ti	$\bar{M}_n (\times 10^{-4})$	$\bar{M}_w (\times 10^{-4})$	\bar{M}_w/\bar{M}_n
1	Cat-A	0	1.8	19.5	10.8
2	Cat-B	0	0.9	15.8	17.6
3	Cat-C	0	1.0	23.8	23.8
4	Cat-D	0	0.58	27.8	47.9
5	Cat-A	5	2.9	26.1	8.9
6	Cat-B	5	2.3	30.9	13.4
7	Cat-C	5	1.8	28.8	16.0
8	Cat-D	5	1.9	42.0	22.1

^a Polymerization conditions: cocatalyst: TEA, Al/Ti = 50, $T = 60^\circ\text{C}$, $t = 30$ min, $\text{H}_2 = 25$ mL, $P_E = 1$ atm, n -heptane = 50 mL, external donor: DDS.

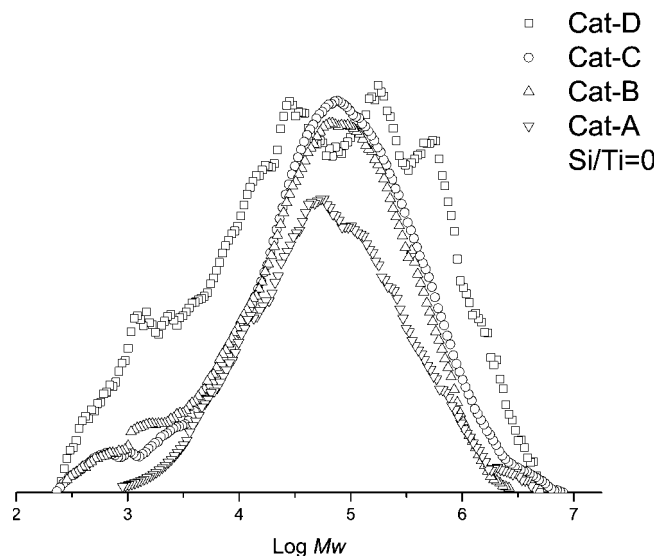


Figure 3 MWD curves of PE obtained from different catalysts.

surface area of the support or enhancement of the disorder of MgCl_2 crystallites by doping with AlCl_3 . The formation of $\text{AlCl}_3/\text{MgCl}_2$ solid solution may also help to fix more TiCl_4 on the support. However, this effect of the doped salt seems to have a limit, as Cat-C showed lower Ti content than Cat-B and the same Ti/Mg ratio as the later.

Ethylene polymerization

The ethylene polymerization activities are shown in Figure 2. It shows that the doped catalysts (Cat-B and Cat-C) exhibit higher activity than the undoped MgCl_2 supported catalyst (Cat-A) in the absence of external donor, while the former catalysts present slightly lower activity than the latter in the presence of DDS. Although the catalyst supported on pure AlCl_3 (Cat-D) presents much lower activity than the other three catalysts, its activity (1320 gPE/gTi-h) is already higher than that of the first generation heterogeneous catalyst based on $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$.¹⁰ This means that AlCl_3 may also act as an active support for titanium chloride, though not so efficient as MgCl_2 . When DDS is used as external donor, the catalyst activity all decreased. It is widely accepted that the addition of electron donor generally decreases polymerization activity because nonstereospecific sites on catalyst are selectively poisoned by external donor.^{11,12}

MW and MWD of polyethylene

The data shown in Table II are MW and MWD of polyethylene obtained with the four catalysts under study. It can be seen that the polydispersity of PE increased strongly with increasing AlCl_3 content in the catalysts.

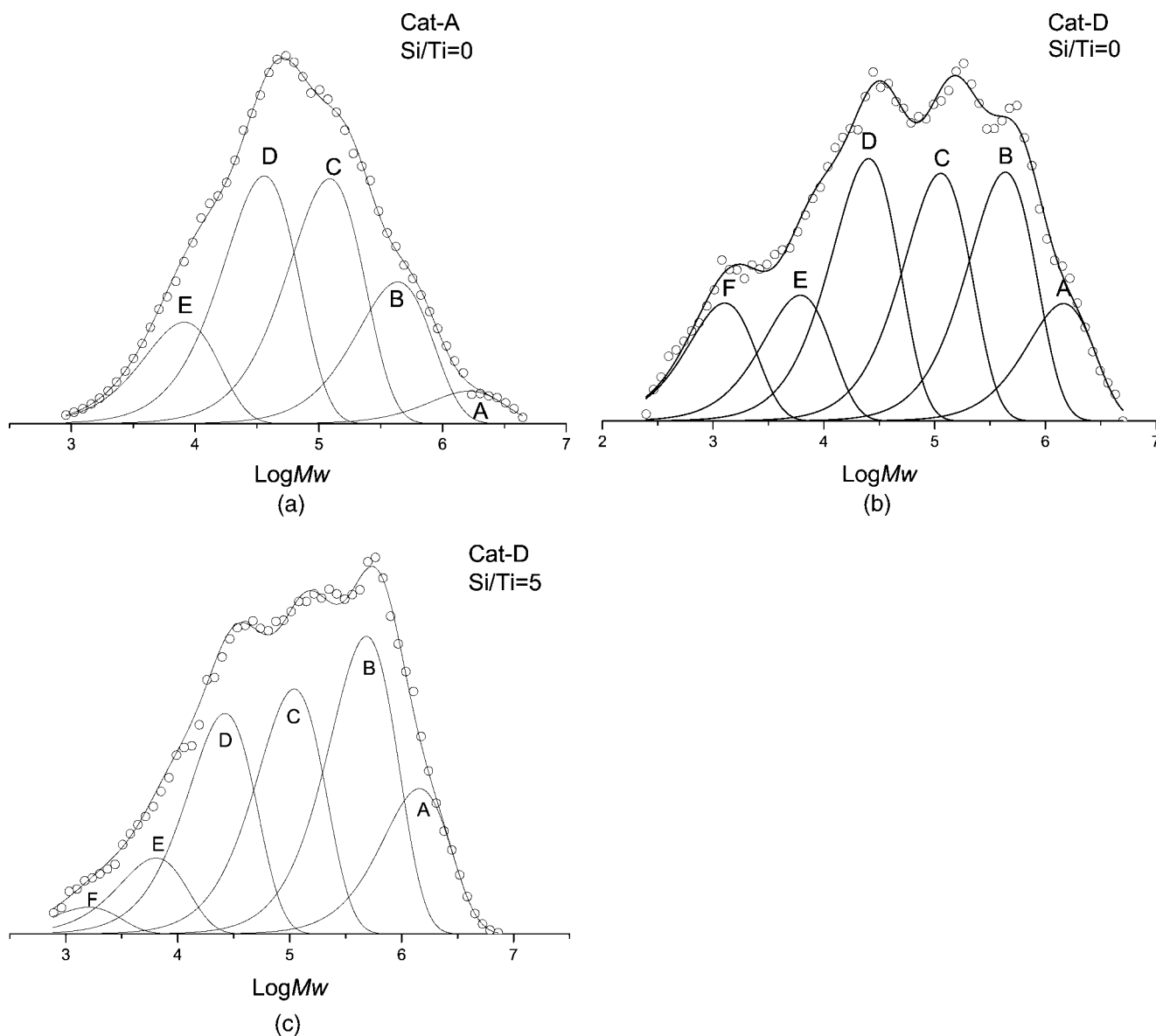


Figure 4 MWD curves of PE and the deconvolution results. (Circles: experimental data; lines: the Flory peaks and their sums).

The MWD of polyethylene obtained with Cat-B, Cat-C and Cat-D, which contain AlCl_3 , is obviously broader than that of Cat-A (free of AlCl_3) (see Fig. 3). The MWD of polyethylene obtained with the AlCl_3 -supported catalyst (Cat-D) is especially broad, with polydispersity index as high as 47.9 in the absence of external donor. The MWD of Cat-D's product has four clearly distinguishable peaks, which is quite unusual. According to Figure 3, MWD of polyethylene can be adjusted over a wide range by varying AlCl_3 content in the catalyst. As shown in Figure 3, when the high-MW fractions increase with increasing AlCl_3 content in catalysts, the low MW fractions ($\text{MW} < 3000$) also increase, forming a low MW "tail." This phenomenon can be explained as the formation of new types of active sites by doping AlCl_3 in MgCl_2 support. Because the contents of very low MW fractions ($\text{MW} < 3000$) and very high MW

fractions ($\text{MW} > 10^6$) in polyethylene produced by Cat-D are much higher than the product of Cat-A, it is reasonable to say that some active sites in Cat-B and Cat-C are formed in similar way as in Cat-D, namely, by anchoring TiCl_4 on AlCl_3 crystallites. The MW of polyethylene basically increases with AlCl_3 content. In addition, the MW and MWD were also influenced by the addition of external donor. The polydispersity index of polyethylene decreased with increasing of Si/Ti molar ratio, on the contrary, the MW increased with increasing of Si/Ti molar ratio, as shown in Table II.

Deconvolution of MWD curves

It has been proved that deconvolution of polymer MWD curves by multiple Flory functions is an effective method to study the ACD of catalyst. Each Flory com-

TABLE III
Deconvolution Results of MWD of Polyethylenes Synthesized by Different Catalyst^a

Run	Catalyst	Si/Ti	$\bar{M}_w/10^4$ (f^b , %)					
			A	B	C	D	E	F
1	Cat-A	0	161.3 (4.1)	42.8 (18.5)	12.1 (32.0)	3.6 (32.4)	0.81 (13.0)	–
2	Cat-B	0	58.0 (12.5)	23.7 (20.7)	8.8 (29.4)	3.0 (22.1)	0.71 (9.9)	0.13 (5.4)
3	Cat-C	0	119.1 (8.2)	34.0 (23.7)	10.4 (30.7)	3.3 (24.9)	0.71 (8.9)	0.10 (3.6)
4	Cat-D	0	143.9 (10.5)	42.9 (22.4)	11.2 (22.3)	2.5 (23.6)	0.61 (11.3)	0.13 (10.0)
5	Cat-A	5	135.1 (8.5)	39.8 (23.4)	11.5 (35.2)	3.8 (24.5)	0.74 (8.5)	–
6	Cat-B	5	114.9 (10.4)	43.9 (28.2)	14.4 (30.6)	4.8 (20.3)	1.3 (7.6)	0.29 (2.8)
7	Cat-C	5	161.3 (9.4)	44.2 (26.3)	12.7 (33.6)	4.2 (22.0)	1.2 (6.3)	0.25 (2.4)
8	Cat-D	5	142.0 (14.5)	47.9 (29.7)	10.9 (24.4)	2.6 (22.0)	0.63 (7.4)	0.17 (2.0)

^a Polymerization conditions of the PE samples are the same as Table II.

^b Percentage of peak area in the whole MWD peak.

ponent is believed to be the MWD curve of polymer produced by one family of active center, with a polydispersity index equal to 2.0.^{8,13}

Figure 4 shows the MWD curves of polyethylene samples and their deconvolution into Flory components. Five or six Flory components can be deconvoluted to fit the MWD of polyethylene in a satisfactory manner. It is worth indicating that the strange MWD curve of polymer produced by Cat-D is also satisfactorily fitted by six Flory components. This may be taken as a good evidence for the rationality of the deconvolution method. Weight average MW and weight percentage of all the Flory components are listed in Table III.

The deconvolution results show that five types of active centers exist in undoped MgCl₂ supported catalyst (Cat-A), while six types of active centers exist in AlCl₃-doped MgCl₂-supported catalysts (Cat-B, Cat-C) and AlCl₃-supported catalyst (Cat-D). Accordingly, it is proved that increase of types of active centers by introducing AlCl₃ into the support should be responsible for the broadening of MWD of polyethylene.

The addition of external donor did not change the number of active center types, but changed the distribution of the Flory components in the whole MWD curve. With addition of external donor, the percentage of the Flory peaks of high MW was increased, while those of low MW were decreased. It means that DDS can selectively poison the active centers (Center D, E, and F), which produce low MW polyethylene.

CONCLUSIONS

Four catalysts with different AlCl₃ content were prepared by the reaction of MgCl₂/AlCl₃-ethanol adduct with TiCl₄. WAXD analysis showed that AlCl₃/MgCl₂ solid solution was formed. The AlCl₃-doped catalysts exhibited slightly higher activity in ethylene polymerization than catalyst supported on pure MgCl₂. MWD of polyethylene is markedly broadened with the increase of AlCl₃ content in the catalysts. The deconvolution of the MWD curves by multiple Flory functions showed that the broadening of MWD of PE is due to increase of types of active centers by introducing AlCl₃ into the support.

References

- Böhm, L. L. *Angew Chem Int Ed* 2003, 42, 5010.
- Cho, H. S.; Chung, J. S.; Lee, W. Y. *J Mol Catal Chem* 2000, 159, 203.
- De Souza, R. F.; Casagrande, O. L., Jr. *Macromol Rapid Commun* 2001, 22, 1293.
- Böhm, L. L. *Macromol Symp* 2001, 173, 53.
- Li, L. D.; Wang, Q. *J Polym Sci Part A: Polym Chem* 2004, 42, 5662.
- Garoff, T.; Leinonen, T. *J Mol Catal Chem* 1996, 104, 205.
- Fregonese, D.; Bresadola, S. *J Mol Catal Chem* 1999, 145, 265.
- Jiang, X.; Chen, Y. P.; Fan, Z. Q.; Wang, Q.; Fu, Z. S.; Xu, J. T. *J Mol Catal Chem* 2005, 235, 209.
- Kashiwa, N. *J Polym Sci Part A: Polym Chem* 2004, 42, 1.
- Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerization*; Academic Press: New York, 1979.
- Lim, S. Y.; Choung, S. J. *J Appl Polym Sci* 1998, 67, 1779.
- Soga, K.; Shiono, T. *Prog Polym Sci* 1997, 22, 1503.
- Kissin, Y. V. *J Polym Sci Part A: Polym Chem* 1995, 33, 227.