

SUPPORTED ZIEGLER-NATTA CATALYSTS FOR ETHYLENE SLURRY POLYMERIZATION AND CONTROL OF MOLECULAR WEIGHT DISTRIBUTION OF POLYETHYLENE

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Abstract The effect of chemical composition of highly active supported Ziegler-Natta catalysts with controlled morphology on the MWD of PE has been studied. It was shown the variation of transition metal compound in the MgCl_2 -supported catalyst affect of MWD of PE produced in broad range: Vanadium-magnesium catalyst (VMC) produce PE with broad and bimodal MWD ($M_w/M_n = 14\text{--}21$). MWD of PE, produced over titanium-magnesium catalyst (TMC) is narrow or medium depending on Ti content in the catalyst ($M_w/M_n = 3.1\text{--}4.8$). The oxidation state of the initial titanium compounds in TMC has only slight effect on MWD of PE produced. Based on MWD data of PE heterogeneity of active centers of TMC and VMC was studied. The results of resolution of experimental GPC curves into Flory components indicated three Flory components are sufficient to describe MWD curve of PE, produced with TMC; six Flory components are required in the case of VMC. In the case of copolymerization of ethylene with 1-hexene over TMC the addition of 1-hexene leads to decrease of MW and to slight effect on M_w/M_n values. On the contrary the strong effect of 1-hexene on MWD of PE produced over VMC was found: the introduction of 1-hexene results in considerable broadening of MWD due to the shifting of the main MWD peak to low MW region. At that comonomer doesn't affect the position of high molecular weight shoulder. The results indicate that some of active centers of VMC producing high MW polymer are not active in the reaction of chain transfer with comonomer.

Keywords: Polyethylene (PE); Vanadium magnesium catalyst (VMC); Titanium magnesium catalyst (TMC); Gel permeation chromatography (GPC); Molecular weight distribution (MWD).

INTRODUCTION

Ziegler-Natta (ZN) type catalysts are widely used in the industry for production of PE with various molecular weights (MWs) and molecular weight distributions (MWDs). There are lots of modifications of ZN catalysts varying in the way of preparation of the support and differences in the active component compound structure and presence of various modifying additives, for example, electron donor compounds used at support or catalyst preparation. The most famous supported ZN type catalysts are titanium-magnesium catalysts (TMC). The active component of these catalysts is titanium chloride supported on the magnesium chloride. Titanium-magnesium catalysts produce PE with narrow and medium MWD; polydispersity values (M_w/M_n) are usually within the range of 4–8^[1, 2]. Vanadium-magnesium catalyst (VMC) containing vanadium chloride as active component supported on the magnesium chloride produce PE with broad MWD; (M_w/M_n) values are usually within the range of 10–25^[3]. One of the most important issues in ethylene polymerization over supported ZN catalysts is the control of MWD of PE. It is supposed that the main reason of MWD broadening ($M_w/M_n > 2$) of olefin

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polymerization over supported ZN catalysts is the heterogeneity of the active centers of these catalysts (multisite catalysts). However, the nature of this heterogeneity remains unclear.

It is important to use the catalyst with optimal morphology at the ethylene slurry polymerization over highly active supported catalysts (small particle size, narrow particle size distribution) to exclude the possible effect of diffusion restrictions on MWD of polymer produced. Only in this case it is possible to get reliable data on the effect of catalysts composition on MWD of polymers. We used in this study the catalysts with controlled morphology (average particle size within the range of 5–10 μm and narrow particle size distribution) prepared according to^[4]. As example the photos of the catalyst particles and PE particles produced over this catalyst are shown in Fig. 1.

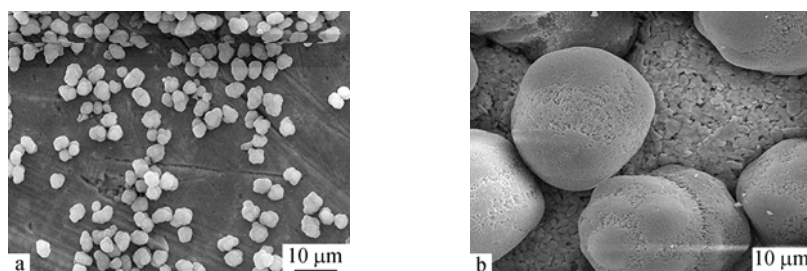


Fig. 1 Photos of the TMC (a) and respective PE (b) particles

In the present paper the data on the effect of chemical composition of the supported ZN catalysts on the MWD of PE are presented. The effects of transition metal compound (Ti, V), Ti content and oxidation state of titanium in TMC on MWD of PE characteristics are discussed.

EXPERIMENTAL

Catalysts were synthesized *via* procedure described previously^[4] by supporting of titanium compounds of different composition (TMC) or VCl_4 (VMC) on highly dispersed magnesium chloride with average particle size 10 μm and narrow particle size distribution.

Three catalysts with Ti content of 0.07 wt% (TMC-0.07), 1.6 wt% (TMC-1.6) and 5 wt% (TMC-5) have been used in this study.

TMC with different titanium oxidation state compounds were obtained by deposition of Ti(II), Ti(III) and Ti(IV) chlorides ($\eta^6\text{-arene-Ti}^{2+}\text{Al}_2\text{Cl}_8$, $\text{Ti}^{3+}\text{Cl}_3 \cdot n\text{DBE}$ (DBE — dibutyl ether), and $\text{Ti}^{4+}\text{Cl}_4$ compounds correspondingly) on highly dispersed magnesium chloride according to reference [5].

Ethylene slurry polymerization was performed in a 0.8 L steel reactor, in heptane, at constant ethylene pressure 4 bar and polymerization temperature 80°C for 1 h; triisobutylaluminium (TIBA) was used as a co-catalyst, its concentration being 2–10 mmol TIBA/L, catalyst concentration was 0.04 g/L.

MWD measurements were performed using a WATERS-150 C instrument in conjunction with Differential Viscometer (Viscotek Model 100). Run conditions were as follows: temperature 140°C; 1,2,4-trichlorobenzene (TCB) was used as a solvent at a flow rate of 1 cm^3/min . Four mixed bed TSK-gel columns (GMHXL-HT, Tosoh Corp.) were used. Calibration was made using narrow Polystyrene standards and PE standards.

Copolymer composition (the content of CH_3 groups) was determined by IR spectroscopy (absorption band at 1378 cm^{-1}) using an IR Fourier spectrometer Shimadzu FTIR 8400S according to reference [6].

RESULTS AND DISCUSSION

Effect of Transition Metal Compound

Table 1 presents the data on the activity of TMC and VMC in ethylene polymerization and MWD of PE produced. It is seen that VMC shows high activity similar to that of TMC. In more detail kinetic data on

ethylene polymerization at different hydrogen concentration over TMC and VMC were published in our previous papers^[2,3].

Table 1. Data on the effect of transition metal compound on the activity of supported ZN catalysts and MWD of PE (80°C, TIBA as cocatalyst)

PE no.	Catalyst type	Content of Ti (V) (wt%)	Activity (kg PE/ g Ti (V) × h × bar C ₂ H ₄)	M_n × 10 ⁻³	M_w × 10 ⁻³	M_z × 10 ⁻³	M_w/M_n	M_z/M_w
1 ^a	TMC	1.6	50	57	210	560	3.7	2.7
2 ^b	VMC	1.8	30	31	440	1800	14	4.1

^a Ethylene pressure 4 bar; [H₂]/[C₂H₄] = 0.25 in gas phase; ^b Ethylene pressure 7 bar; [H₂]/[C₂H₄] = 0.07 in gas phase

Table 1 and Fig. 2 present SEC data for PE synthesized with VMC and TMC. The great difference between PE produced over VMC and TMC is observed. Vanadium-magnesium catalysts produced PE with broad and bimodal MWD. M_w/M_n value for PE synthesized with VMC is equal to 14, in contrast to 3.7 for PE synthesized with TMC. The MWD curve for PE produced with VMC demonstrates explicit shoulder within the high-MW region.

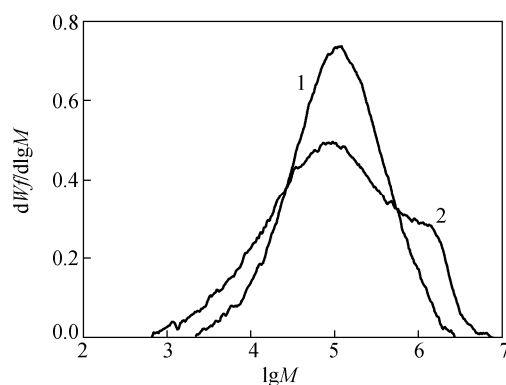


Fig. 2 MWD curves of PE samples, produced over TMC (curve 1) and VMC (curve 2) (polymerization conditions see in Table 1)

Experimental data on the effect of catalyst composition on the MWD of PE was used for analysis of heterogeneity of active centers of TMC and VMC. For that analysis we used the approach based on resolution of experimental GPC curves into Flory components according to Ref. [7]. Two PE samples (from Table 1)

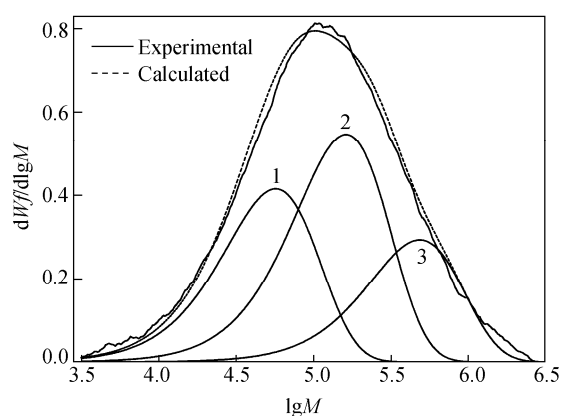


Fig. 3 MWD curve of PE sample produced with TMC (Table 1 exp. 1) and its resolution into Flory components

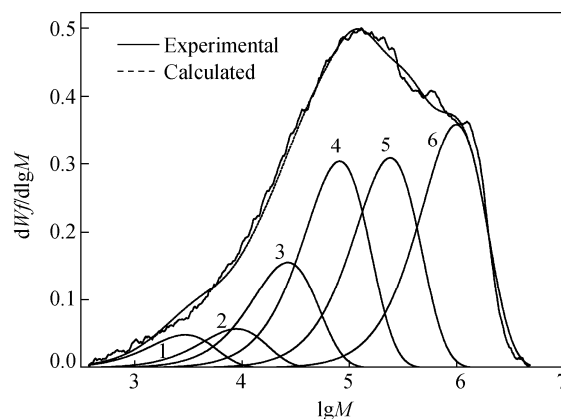


Fig. 4 MWD curve of PE produced with VMC (Table 1, exp. 2) and its resolution into Flory components

produced over TMC and VMC were analyzed. The results of resolution of GPC curves into Flory components are presented in Figs. 3, 4 and Table 2. The data indicate three Flory components are sufficient to describe MWD curve of PE, produced with TMC (Fig. 3). This result is in agreement with our previous experimental data obtained at analysis of heterogeneity of active centers of TMC by fractionation of PE into fractions with narrow MWD with $M_w/M_n \leq 2$ ^[8]. It was found that three components corresponding to three groups of active centers are sufficient for proper fitting of experimental MWD curve of PE obtained over TMC with different Ti content. Analysis the MWD of PE, produced with VMC is more complicated. Six Flory components are required in this case (Fig. 4, Table 2).

Table 2. Data on calculated MWD parameters of PE

PE ^a no.	Catalyst	Flory component ^b	Portion of Flory component (%)	$M_w \times 10^{-3}$
1	TMC	1	33.4	58
		2	43.9	160
		3	23.7	475
2	VMC	1	3.9	3
		2	4.6	9
		3	12.5	27
		4	24.4	81
		5	24.8	240
		6	28.8	990

^a PE numbers are corresponds to those in Table 1 and Fig. 2;

^b Flory components numbers and MWD curves are shown on Figs. 3, 4.

Control of MWD of PE via Variation of Chemical Composition of Ti Based Catalysts

Effect of the support (MgCl₂) and Ti content in supported catalysts on MWD of PE produced

The data on the effect of Ti content on the activity of TMC and MWD of PE are presented in Table 3. The activity of TMC-0.07 is about ten times higher then that of TMC-5. It was shown^[2] that the reason of higher activity of TMC with low Ti content is the higher number of the active centers. The similar Kp values at ethylene polymerization over TMC with different Ti content (0.1 wt% and 0.9 wt% of Ti) were found^[9].

Table 3. Data on the effect of Ti content on the catalysts's activity ^a and MWD of PE

Catalyst	PE no.	Ti content (wt%)	Activity (kg PE/g Ti × h × bar C ₂ H ₄)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
TMC (0.07) ^b	1	0.07	460	57	180	3.1
TMC (5) ^b	2	5.0	48	58	280	4.8
δ-TiCl ₃ ^c	3	27.5	2.0	40	270	6.8

^a Polymerization conditions: 80°C, TIBA, ethylene pressure 4 bar, [H₂]/[C₂H₄] = 0.25;

^b The numbers correspond to the content of Ti; ^c Commercial sample of Solvay type nonsupported catalyst

The increase of titanium content in TMC results in the increase of M_w value of PE (M_w increases from 180×10^3 up to 280×10^3) and increase of M_w/M_n value from 3.1 to 4.8 (exp. 1 and 2 in Table 3). M_n values change slightly and remain within the range of 57×10^3 – 58×10^3 . It is seen that the MWD broadening arises from the high-molecular-weight part of PE (see curves 1 and 2 in Fig. 5).

Data on the polymer obtained at ethylene polymerization over non-supported δ-TiCl₃ catalyst are presented in Table 3 and Fig. 5 as well. It is seen that δ-TiCl₃ catalyst produces PE with broader MWD in comparison with supported TMC catalysts. This broadening is caused by formation of both low-molecular and high-molecular parts of PE (compare curves 1 and 3, Fig. 5).

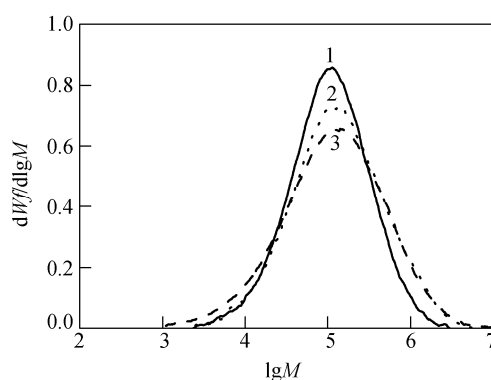


Fig. 5 MWD curves of PE produced over TMC with different Ti content and δ -TiCl₃ catalyst. Curves numbers correspond to PE numbers in Table 3.

Effect of the oxidation state of Ti in TMC composition on the activity and MWD of PE produced

It is supposed that the main reason of MWD broadening ($M_w/M_n > 2$) is heterogeneity of the active centers of ZN catalysts (multisite catalysts). Some authors^[10, 11] relate a broad MWD of PE produced with TMC to the formation of various active sites containing Ti(II), Ti(III) and Ti(IV) compounds. In this study, we investigated the influence of oxidation state of titanium in titanium compounds on the catalytic properties of MgCl₂-supported catalysts in ethylene polymerization and on MWD of PE produced. Soluble compounds of titanium in different oxidation states (η^6 -arene-Ti²⁺Al₂Cl₈, Ti³⁺Cl₃nDBE, and Ti⁴⁺Cl₄) were synthesized according to reference [5], analyzed by ESR and ¹³C-NMR methods, and adsorbed on the highly dispersed magnesium chloride (Table 4).

Table 4. Effect of the oxidation state of Ti in TMC on catalyst's activity^a and MWD of PE

Catalyst	I	II	III
Titanium compound	[η^6 BenzeneTiAl ₂ Cl ₈]	TiCl ₃ nDBE	TiCl ₄
Ti content (wt%)	0.7	1.0	0.9
Ti oxidation state in Ti compound	Ti(II)	Ti(III)	Ti(IV)
Possible oxidation state of active center	Ti ²⁺	Ti ³⁺ , Ti ²⁺	Ti ⁴⁺ , Ti ³⁺ , Ti ²⁺
Activity (kg PE/g Ti h)	430	170	280
$M_w \times 10^{-3}$	310	280	280
M_w/M_n	5.2	4.7	4.7

^a Polymerization conditions: heptane, 80°C, TIBA as cocatalyst, ethylene pressure 4 bar, hydrogen pressure 1 bar, for 1 h

TMC obtained by deposition of Ti(II), Ti(III) and Ti(IV) chlorides on a highly dispersed magnesium chloride (catalysts I, II, III in Table 4) were tested in ethylene polymerization. Table 4 presents the data on the catalyst activity and MWD of PE produced.

Catalyst I containing divalent titanium shows the activity in ethylene polymerization in the absence of organo-aluminum co-catalyst (11 kg/g Ti h bar C₂H₄) (80°C). This result confirms that catalyst I actually contains a divalent titanium compound as the active component, since according to the literature data, divalent titanium compounds are active in ethylene polymerization without organo-aluminum co-catalyst^[12, 13]. Note that activity of the supported catalyst obtained in our study (11 kg/g Ti h bar C₂H₄) is approximately two orders of magnitude higher as compared to the activity of bulk TiCl₂ (0.16 kg/g Ti h bar C₂H₄)^[13]. The data of Table 4 show that catalyst I containing a Ti(II) compound shows a maximum activity. Presumably, this relates to a more dispersed state of the active component in this catalyst due to formation of titanium dichloride complexes with aluminum chlorides. Catalyst II of TiCl₃nDBE/MgCl₂ composition is less active as compared to conventional catalyst III of TiCl₄/MgCl₂ composition. This may be caused by partial blocking of the active sites by DBE. Previously, it was shown in reference [14] that catalysts TiCl₄/MgCl₂ and TiCl₃/MgCl₂, being free of ether, have

close activities.

As seen from Table 4, catalysts I, II and III, containing titanium chlorides in different oxidation states, in the presence of TIBA as cocatalyst produce PE with a close MW and MWD values ($M_w/M_n = 4.7\text{--}5.5$).

Thus catalysts I, II, III produce PE with the similar (broad) MWD ($M_w/M_n = 3.9\text{--}5.2$). It means possible formation of active centers in the different oxidation states of Ti is not the real reason of the broad MWD of PE produced over TMC.

Effect of Comonomer (1-Hexene) on the MWD of Polymers Produced over TMC and VMC.

Earlier we have studied copolymerization of ethylene with α -olefins over supported ZN catalysts of different composition^[15]. It was shown VMC have much higher copolymerizing reactivity in comparison with TMC. Here we present the data on the effect of 1-hexene on MWD of copolymers prepared with TMC and VMC.

Table 5 and Figs. 6, 7 present the data on ethylene-1-hexene copolymerization initiated by TMC and VMC. The data indicate very different effect of 1-hexene on MWD of copolymers produced. In the case of copolymerization over TMC, addition of 1-hexene proceeds to decrease of MW and to slight effect on the M_w/M_n value. In the case of VMC the data indicate on the strong effect on MWD: the introduction of 1-hexene results in considerable broadening of MWD: while the main MWD peak is shifted to low MW region, the high MW shoulder stays at the same position (Fig. 7). As a result, M_w/M_n and M_z/M_w values are increased (Table 5).

Table 5. Data on ethylene-1-hexene copolymerization^a over ZN catalysts with different composition

Polymer no.	Catalyst	C ₆ H ₁₂ /C ₂ H ₄ ^b	Activity (kg/g Ti × h × bar)	MI(5) (g/10 min)	$M_w \times 10^{-3}$	M_w/M_n	C ₆ H ₁₂ ^c (mol%)
1	TMC-0.07	0	450	0.13	310	3.3	0
2		2.6	1020	0.41	220	3.5	1.9
3	TMC-5	0	33	0.11	370	4.8	0
4		2.6	130	0.5	220	4.3	1.5
5	VMC	0	26	0.15	440	14	0
6		0.40	56	1.7	430	20.5	1.2

^a Polymerization conditions: 80°C, TIBA as cocatalyst, ethylene pressure = 2 bar in exps. 1–4 and 7 bar in exps. 5, 6; the ratio H₂/C₂H₄ = 0.13 in exps. 1–4 and 0.07 in exps. 5, 6;

^b Comonomer concentration ratio in heptanes; ^c 1-Hexene content in copolymer

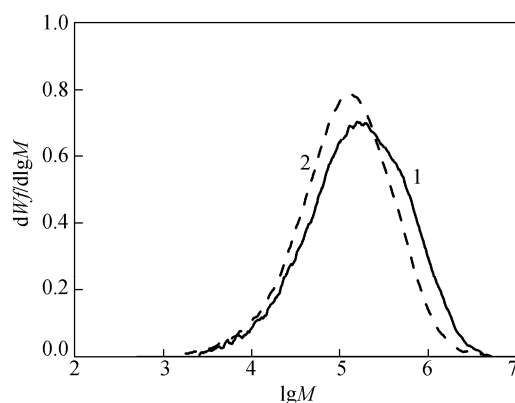


Fig. 6 Effect of 1-hexene on MWD of PE produced over TMC-5 (curves 1 and 2 are correspond to exps. 3 and 4 Table 5)

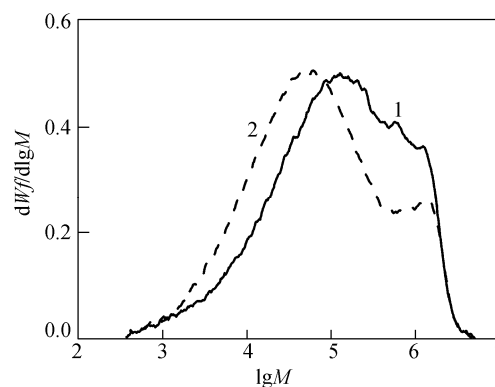


Fig. 7 Effect of 1-hexene on MWD of PE produced over VMC (curves 1 and 2 are correspond to exps. 5 and 6 Table 5)

The results indicate that some of active centers of VMC producing high MW polymer are not active in the reaction of chain transfer with comonomer.

In our previous paper we proved the heterogeneity of VMC active centers for the reaction of chain transfer with hydrogen^[3]. Data presented here indicates heterogeneity of VMC active centers for the reaction of chain

transfer with 1-hexene. Similar to the hydrogen effect, the VMC contains two types of active centers, one of them is active in the chain transfer reaction with 1-hexene. These centers produce polymer with lower MW at copolymerization with 1-hexene. Another type of active centers is not active in the chain transfer reaction with 1-hexene. These centers produce high MW PE ($M_w = 1 \times 10^6 - 3 \times 10^6$) and comonomer doesn't affect the position of high molecular weight shoulder (Fig. 7).

CONCLUSIONS

Transition metal compound in the $MgCl_2$ -supported ZN catalyst affect of MWD of PE produced in broad range: VMC produce PE with broad and bimodal MWD ($M_w/M_n = 14-21$). MWD of PE, produced over TMC is narrow or medium depending on Ti content in the catalyst ($M_w/M_n = 3.1-4.8$). Non supported δ - $TiCl_3$ catalyst produces PE with broader MWD ($M_w/M_n = 6.8$) in comparison with supported TMC catalysts.

Heterogeneity of active centers of TMC and VMC was studied based on detailed analysis of MWD data of PE produced. The results of resolution of GPC curves into Flory components indicated three Flory components are sufficient to describe MWD curve of PE, produced with TMC. Six Flory components are required in the case of VMC. It indicates on higher heterogeneity of active centers VMC in comparison with TMC.

TMC containing the initial titanium compounds with different titanium oxidation state (Ti(II), Ti(III), Ti(IV)) produce PE with a close M_w and MWD values ($M_w/M_n = 4.7-5.2$). Probably possible formation of active centers in the different oxidation states of Ti is not the real reason of the broad MWD of PE produced over TMC.

Completely different effect of comonomer (1-hexene) on the MWD of polymer produced over TMC and VMC have been found. In the case of copolymerization of ethylene with 1-hexene over TMC the addition of 1-hexene leads to decrease of MW and to slight effect on M_w/M_n values. In contrary the introduction of 1-hexene at ethylene polymerization over VMC results in considerable broadening of MWD due to the shifting of the main MWD peak to low MW region. At the same time comonomer doesn't affect the position of high molecular weight shoulder. The results indicate that some of active centers of VMC producing high MW polymer are not active in the reaction of chain transfer with comonomer.

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