

Supported Titanium–Magnesium Catalysts with Different Titanium Content: Kinetic Peculiarities at Ethylene Homopolymerization and Copolymerization and Molecular Weight Characteristics of Polyethylene

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ABSTRACT: The effect of Ti content on the activity of titanium–magnesium catalysts (TMC) and molecular weight distribution (MWD) of polyethylene (PE) produced has been studied. It was found that the activity enhances sharply as Ti content decreases from 0.6 to 0.07 wt %, and shows no significant changes in the Ti content range of 0.6–5.0 wt %. The maximum activity (36 kg PE/mmol Ti × h × bar C₂H₄) was observed for TMC with the lowest Ti content. The catalyst with low titanium content (~ 0.1 wt % of Ti) produced PE with narrower MWD ($M_w/M_n = 3.1$ – 3.5) as compared to catalysts with higher titanium content (3–5 wt % of Ti; $M_w/M_n = 4.8$ – 5.0). New data on the effect of hydrogen on MWD of PE have been found. Increasing hydrogen concentration results in broadening the MWD of PE, especially in the case

of TMC with high titanium content. The data presented indicate the heterogeneity of active centers of TMC in the reaction of chain transfer with hydrogen. The data on the ethylene–hexene-1 copolymerization over TMC with different titanium content are presented. Comonomer reactivity ratios were shown to be independent of the Ti content in TMC. Presumably the difference in activity of these catalysts is mainly caused by the difference in the number of active centers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5436–5442, 2006

Key words: ethylene polymerization; gel permeation chromatography (GPC); molecular weight distribution (MWD); polyethylene (PE); size exclusion chromatography (SEC); titanium–magnesium catalyst

INTRODUCTION

One of the most important problems in ethylene polymerization over highly active supported Ziegler–Natta catalysts is the control of molecular weight (MW) and molecular weight distribution (MWD) of polyethylene (PE). The most famous supported Ziegler–Natta type catalysts are titanium–magnesium catalysts (TMC), which are widely used in industry for the production of PE with various MW and MWD. The active component of these catalysts is titanium chloride supported on magnesium chloride. There is a lot of TMC modifications varying in the way of support preparation and differing in terms of the titanium compound structure and the presence of various modifying additives, for example, electron donor compounds used for support or catalyst preparation. However, the information about the effect of catalyst composition on MW and MWD of PE is scarce, and is mainly discussed in the patent literature. Some data on the TMC composition

and possibilities to control MW and MWD of PE produced over TMC are presented in the review.¹ 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 It is supposed that the reason for MWD broadening ($M_w/M_n > 2$) is heterogeneity of the active centers of these catalysts (multisite catalysts). However, the nature of this heterogeneity remains unclear. The analysis of MWD curves of the polyethylene produced with the use of one of TMC modifications is presented in the articles.^{2,3} It was assumed that there are several types of the active centers differing in their reactivity.

Earlier, we have obtained the data on sharp increase of TMC activity (based on the unit of titanium weight) that occurs when titanium content in catalysts decreases to less than 0.2 wt %.⁴ However, the data on MW and MWD of polyethylene produced using these catalysts are absent. We have now investigated ethylene polymerization over one of the newly developed TMC modifications.⁵ These catalysts have the spherical shape of particles and a narrow particle size distribution; they allow producing PE with the improved morphology (spherical particles with a narrow particle size distribution and a higher bulk density of PE

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powder) when compared with the catalysts studied elsewhere.⁴

In the present article, the data on the effect of Ti content (in the range of 0.07–5.0 wt %) and hydrogen concentration on TMC activity in ethylene polymerization and MWD of PE are presented and discussed along with the data on copolymerization of ethylene with hexene-1 over catalysts with different titanium content.

EXPERIMENTAL

The catalysts were synthesized via the procedure described elsewhere⁵ by supporting titanium tetrachloride on highly dispersed magnesium chloride. The support was prepared by the interaction of PhSiCl_3 with organomagnesium compound ($\text{MgPh}_2 \times 0.5 \text{ MgCl}_2$) dissolved in the mixture of phenyl chloride and dibutyl ether. The support was washed with heptane and used for preparation of the catalysts with various titanium contents. The supported catalyst containing 0.6 wt % of titanium (TMC-0.6) was prepared through the reaction of a calculated amount of TiCl_4 with the slurry of Mg-containing support at 60°C. The catalysts containing 1.6 wt % of titanium (TMC-1.6), 3 wt % of titanium (TMC-3), and 5 wt % of Ti (TMC-5) were prepared through the reaction of excess TiCl_4 (molar ratio Ti/Mg being 1) at 60, 100, and 128°C, accordingly. Preparation of the catalysts with low titanium content (0.07 and 0.1 wt % of Ti; catalysts TMC-0.07 and TMC-0.1) included preliminary treating of the support with AlEt_2Cl and carbon tetrachloride at 25°C followed by washing with heptane. The catalysts TMC-0.07 and TMC-0.1 were made through the reaction of a calculated amount of TiCl_4 with the prepared support at 40°C. All catalysts were washed with heptane at 25°C.

The obtained catalysts had the spherical shape with the average particle size of 10 micron, and a narrow particle size distribution.

The titanium contents in catalysts were determined by AES-ICP using an Optima 4300 DV spectrometer.

Ethylene slurry polymerization

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 cocatalyst, its concentration being 2–10 mmol TIBA/L, the catalyst concentration was 0.04 g/L. Hydrogen was used as a chain transfer agent to control MW of PE. At ethylene–hexene-1 copolymerization, co-monomer was introduced once at the beginning of the experiment. Copolymer yield was limited so as to prevent the change of hexene-1 concentration over 15 wt %.

MWD measurements

MWD measurements were performed using a WATERS-150 C instrument in conjunction with a differential viscometer (Viscotek Model 100). Run conditions were as follows: temperature 140°C; 1,2,4-trichlorobenzene (TCB) used as a solvent at a flow rate of 1 cm^3/min . Four mixed bed TSK-gel columns (GMHXL-HT, Tosoh) were used. Conventional ($\log \{MW\}$ versus retention volume) and universal ($\log \{MW \times [\eta]\}$ versus retention volume) calibrations were made using narrow polystyrene standards and PE standards. Homopolymer samples under study were linear HDPE, and we registered good correspondence of conventional and universal calculation data; here we present the results of GPC using conventional calibration.

RESULTS AND DISCUSSION

Homopolymerization of ethylene over TMC with different Ti content

The effect of Ti content on the catalyst activity

Data on the effect of titanium content on the activity of TMC are given in Table I (polymerization with hydrogen at $\text{H}_2/\text{C}_2\text{H}_4 = 0.25$ and polymerization without hydrogen). The activity of catalysts based on the unit

TABLE I
Data on the Effect of Ti Content on the Activity of TMC, MW, and MWD of PE
(80°C, Ethylene Pressure 4 Bar, TIBA as Cocatalyst)

Catalyst no.	Content of Ti (wt %)	Activity ^a (kg PE/ $\text{gTi} \times \text{h} \times \text{bar C}_2\text{H}_4$)	Activity ^b (kg PE/ $\text{gTi} \times \text{h} \times \text{bar C}_2\text{H}_4$)	MI(5) ^c (g/10 min)	M_n (10^{-3})	M_w (10^{-3})	M_z (10^{-3})	M_w/M_n	M_z/M_w
1	0.07	710	460	0.80	57	180	420	3.1	2.4
2	0.1	760	475	0.80	57	200	540	3.5	2.7
3	0.6	110	50	0.55	58	220	630	3.8	2.8
4	1.6	–	50	0.50	57	210	560	3.7	2.7
5	3	83	34	0.35	50	250	810	5.0	3.2
6	5	56	48	0.21	58	280	940	4.8	3.4

^a Polymerization without hydrogen.

^b Polymerization at the ratio $[\text{H}_2]/[\text{C}_2\text{H}_4] = 0.25$ in the gas phase; the MI and MW data are obtained for polymers prepared in these experiments.

^c Melt index at load 5 kg (190°C).

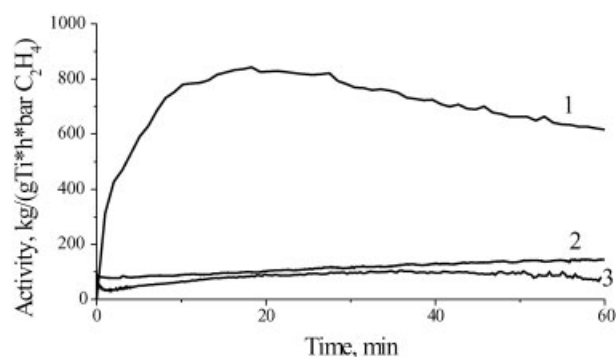


Figure 1 Kinetic profile of ethylene polymerization without hydrogen over TMC with different Ti content: curve 1, TMC-0.1; curve 2, TMC-0.6; curve 3, TMC-3 (see Table I, Experiments 2, 3, and 5, accordingly).

of titanium weight varies insignificantly when titanium content ranges from 0.6 to 5 wt %, and makes up 34–50 kg PE/(gTi \times h \times bar C₂H₄) (polymerization with hydrogen). However, the activity grows sharply as titanium content decreases to 0.1–0.07 wt %, and reaches 475 kg PE/(gTi \times h \times bar C₂H₄) (polymerization with hydrogen) and 760 kg PE/(gTi \times h \times bar C₂H₄) (polymerization without hydrogen). The shape of kinetic curves is virtually independent of titanium content in the catalysts (Fig. 1). The activity increases at the initial stage (for 10–20 min), and then it remains stable for one hour, with a slight decrease being possible.

As we mentioned earlier, the similar data on the effect of titanium content on TMC activity for polymerization without hydrogen have been reported.⁴ The activity of catalysts did not change significantly when titanium content decreased from 1.2 to 0.4 wt %. However, the activity increased sharply with the decrease of titanium content from 0.2 to 0.05 wt %, and attained 360–670 kg PE/gTi \times h \times bar C₂H₄) at the titanium content of 0.1–0.05 wt %.

Recently⁶ the number of active centers (C_p) and propagation rate constants (K_p) at ethylene polymerization over TMC with the low titanium content (0.1 wt %) prepared accordingly⁴ have been determined using the method of polymerization inhibition by ¹⁴CO. The activity of this catalyst was 250 kg PE/(gTi \times h \times bar C₂H₄). It was found that the number of active centers for this catalyst makes 0.18 mol/mol Ti. The value of K_p does not differ significantly from the one registered for TMC samples with titanium content varying in the range of 0.8–1.2 wt %, which equals 1.2×10^4 L/mol \times s.⁶ These data evidence that the sharp increase of activity for the catalysts with the low titanium content is caused by increased number of the active centers.

We calculated the number of active centers taking the value of $K_p = 1.2 \times 10^4$ L/mol \times s and the data on the activity for catalysts with different titanium content presented in Table I. For the catalyst TMC-5,

which has the activity of 56 kg PE/gTi \times h \times bar C₂H₄ at ethylene polymerization without hydrogen, the number of active centers equals 0.04 mol/mol Ti, while for TMC-0.1 sample, which has the activity of 760 kg PE/gTi \times h \times bar C₂H₄, the number of active centers reaches 0.55 mol/mol Ti. Thus, in highly active catalysts with low titanium content, a considerable fraction of titanium is the active centers in ethylene polymerization.

Note that the activity of TMC-0.1 catalyst at ethylene polymerization is extremely high (760 kg PE/(gTi \times h \times bar C₂H₄)) (36 kg PE/(mmolTi h bar C₂H₄)) and greatly exceeds the activity of titanocenes and Ti-phenoxo-imine complexes supported on MgCl₂ \times *n*AlR_x(OR)_{3-x} (2.9–9.1 kg PE/mmolTi \times h \times bar C₂H₄).⁷

The data on and MWD of PE produced over the catalysts with different titanium content are given in Table I. Polymerization was performed in the presence of hydrogen at the ratio of H₂/C₂H₄ = 0.25 (in the gas phase). It is seen that the increase of titanium content in TMC results in the increase of M_w values of polyethylene (from 180×10^3 up to 280×10^3). However, M_n values change only slightly and remain within the range of $(50\text{--}58) \times 10^3$. A significant broadening of MWD is seen at the increase of titanium content in TMC, especially for TMC-3 and TMC-5 catalysts (M_w/M_n values increased from 3.1 up to 4.8–5.0, M_z/M_w values changed from 2.4 to 3.4). MWD curves for PE produced with TMC-0.07 and TMC-3 catalysts are presented in Figure 2 as an example. It is seen that the MWD broadening arises from the high-molecular-weight part of PE.

Thus, the data on the effect of titanium content on MWD of PE indicate that catalysts with higher titanium content (3–5 wt %) have a higher heterogeneity of the active centers, which is evidenced by broadening of the MWD of PE. It can be supposed that titanium compounds with lower oxidation states of titanium are formed in these systems, and therefore the PE with higher MW is obtained.¹ At the same

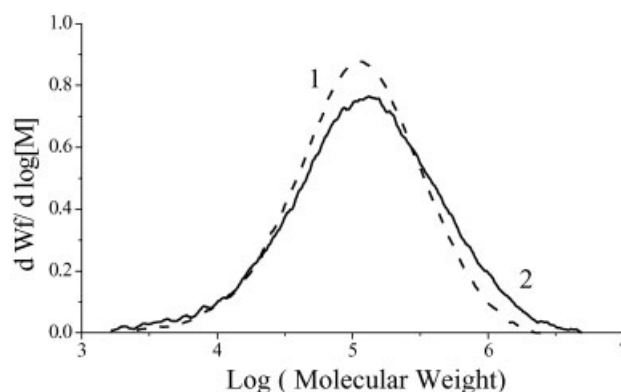


Figure 2 MWD data for PE produced over TMC-0.07 (curve 1) and TMC-3 (curve 2) (polymerization at [H₂]/[C₂H₄] = 0.25) (see Table I, Experiments 1 and 5).

TABLE II
Data on the Effect of Hydrogen on MWD of PE Produced over TMC-0.07
(Experiments 1–5) and TMC-5 (Experiments 6–10) Catalysts
(Ethylene Pressure 4 Bar, TIBA as Cocatalyst)

Exp. No.	[H ₂]/[C ₂ H ₄]	Activity (kg PE/gTi × h × bar)	MI(5) ^d (g/10 min)	M _n (10 ⁻³)	M _w (10 ⁻³)	M _z (10 ⁻³)	M _w /M _n	M _z /M _w
1 ^a	0	711			1800 ^c			
2 ^a	0.25	460	0.80	57	180	424	3.1	2.4
3 ^a	0.5	260	2.2	41	140	330	3.3	2.4
4 ^a	1	170	15	20.5	84	220	4.1	2.6
5 ^a	1.25	160	28	17	66	150	3.9	2.3
6 ^b	0	56			2800 ^c			
7 ^b	0.25	48	0.20	58	280	940	4.8	3.4
8 ^b	0.5	34	0.70	43	210	705	4.9	3.3
9 ^b	1	26	4.2	17	130	650	7.7	5
10 ^b	1.5	24	9.0	12	100	470	8.3	4.7

^a Catalyst TMC-0.07.

^b Catalyst TMC-5.

^c Viscosity-average molecular weight (M_v) calculated from [η] data (11 and 15 dL/g for Experiments 1 and 6 accordingly) (135°C, decalin).

^d Melt index at load 5 kg (190°C).

time, the catalysts with lower titanium content and higher activity allow producing PE with narrow MWD ($M_w/M_n = 3.1$ – 3.5).

Ethylene polymerization in the presence of hydrogen: The data on molecular weight distribution of PE

The data on the effect of hydrogen on the activity of TMC with different titanium content (TMC-0.07 and TMC-5) are presented in Table II. It is seen that the addition of hydrogen at the ratio of $H_2/C_2H_4 = 0.25$ – 0.5 results in a significant reduction of activity of TMC-0.07 catalyst (Table II, Experiments 1–3). With the further increase of hydrogen content, the activity slightly reduces and finally gets stable on the level of 160 kg PE/gTi × h × bar C₂H₄) at molar ratio $H_2/C_2H_4 = 1.25$, which is high enough. In the case of TMC-5 catalyst, the addition of hydrogen decreases the catalyst activity to a smaller degree. However, the activity of TMC-0.07 catalyst is much higher than that of the catalyst TMC-5 in all cases observed. Kinetic curves for ethylene polymerization using TMC-0.07 and TMC-5 catalysts with and without hydrogen are shown in Figure 3. The catalysts are stable enough in ethylene polymerization with the duration of 1 h.

The effect of hydrogen on the activity of ethylene polymerization over TMC is well-known and is discussed in the literature.^{1–3,8–10}

The data on the effect of hydrogen content (H_2/C_2H_4 ratio) on MW and MWD of PE produced on the catalysts with different titanium content are also given in Table II. It is evident that the increase of hydrogen content decreases MW of PE. Note that MW of the PE produced on TMC-0.07 (M_w value) is lower than that of the PE produced on TMC-5 (compare the experi-

ments at the same H_2/C_2H_4 ratio: Experiments 2 and 7; 3 and 8; 4 and 9).

We have observed the new effect of hydrogen content on MWD of PE for both catalysts, the M_w/M_n values increased with increasing hydrogen content. However, the extent of this effect varies for the catalysts with different titanium content. In the case of TMC-0.07, a rather small increase of M_w/M_n values was observed (from 3.1 up to 4.1, see Table II, Experiments 1–5). For TMC-5 catalyst, an increase in M_w/M_n values was much more pronounced (from 4.8 up to 8.3, see Table II, Experiments 6–10). As a result, the highest differences in M_w/M_n values were observed in the experiments on ethylene polymerization over TMC-0.07 and TMC-5 at high hydrogen concentration

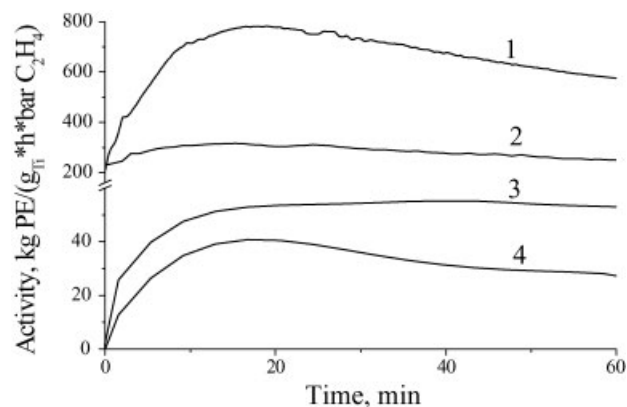


Figure 3 Kinetic profile of ethylene polymerization without hydrogen and with hydrogen over TMC-0.07 (curves 1 and 2) and TMC-5 (curves 3 and 4) (Experiments 1 and 3: polymerization without H₂ (see Table II, Experiments 1 and 6); Experiments 2 and 4: polymerization at $[H_2]/[C_2H_4] = 0.5$ in the gas phase (see Table II, Experiments 3 and 8)).

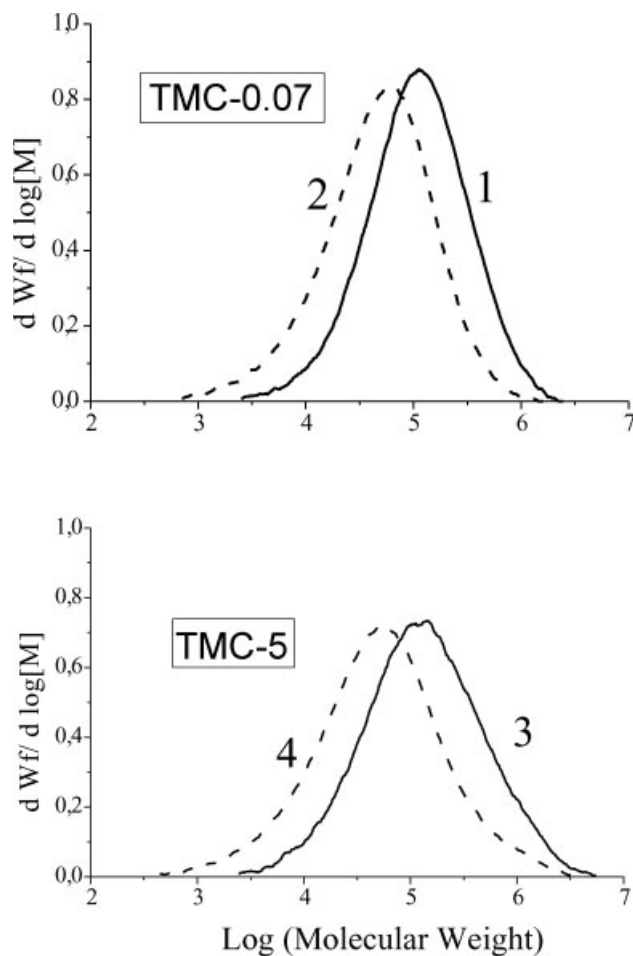


Figure 4 The effect of hydrogen concentration on MWD of PE produced over TMC with different Ti-content: curves 1 and 3, $[H_2]/[C_2H_4] = 0.25$ (see Table II, Experiments 2 and 4); curves 2 and 4, $[H_2]/[C_2H_4] = 1.0$ (see Table II, Experiments 7 and 9).

($H_2/C_2H_4 = 1-1.5$) ($M_w/M_n = 3.9-4.1$ for TMC-0.07 and 7.6–8.3 for TMC-5). The corresponding MWD curves are presented in Figure 4. One can see that as H_2 concentration increased, the MWD peaks shifted to the low molecular weight region except for high molecular weight tail. This effect is more pronounced in the case of TMC-5 catalyst [Fig. 4(b)]. It means that hydrogen similarly affects MW of PE produced on the most part of active centers of TMC except for high MW component.

It is generally supposed in the literature that the heterogeneity of the active centers that leads to broadening of MWD of PE is related to their different reactivity in the propagation reaction.^{2,3} However, the data presented here suggest the heterogeneity of active centers of TMC in the reaction of chain transfer with hydrogen.

The data on the effect of hydrogen concentration on MW of PE (M_n values, Table II) were used to calculate the ratios the rate constants of chain transfer reaction with hydrogen (K_{tr}^H) and the propagation reaction

(K_p). It should be noted that determinate K_{tr}^H/K_p values are the average data describing a combination of active centers with different reactivities. The calculations were made using the known eq. (1) from Ref. 11.

$$1/P_n - 1/P_n^0 = \{K_{tr}^H/K_p \times [C_2]\} \times [H_2]^n \quad (1)$$

Here, P_n is the degree of polymerization, P_n^0 is the degree of polymerization at polymerization without hydrogen, $[C_2]$ and $[H_2]$ are the concentrations of ethylene and hydrogen, and n is the order of transfer reaction with hydrogen.

MW of PE produced without hydrogen is very high and P_n^0 value could not be measured by SEC; so the P_n^0 value was calculated from the data on viscosity-average M_w (M_v value):

$$P_n^0 = M_v/(28 \times D), \quad (2)$$

where M_v is the viscosity-average M_w , $D = M_w/M_n$.

The M_v data are shown in Table II (Experiments 1 and 6). The polydispersity (D value) was assumed to be based on the data for ethylene polymerization with the minimal hydrogen concentration (Table II, Experiments 2 and 7). First we evaluated the order of transfer reaction with hydrogen using eq. (1). Figure 5(a)

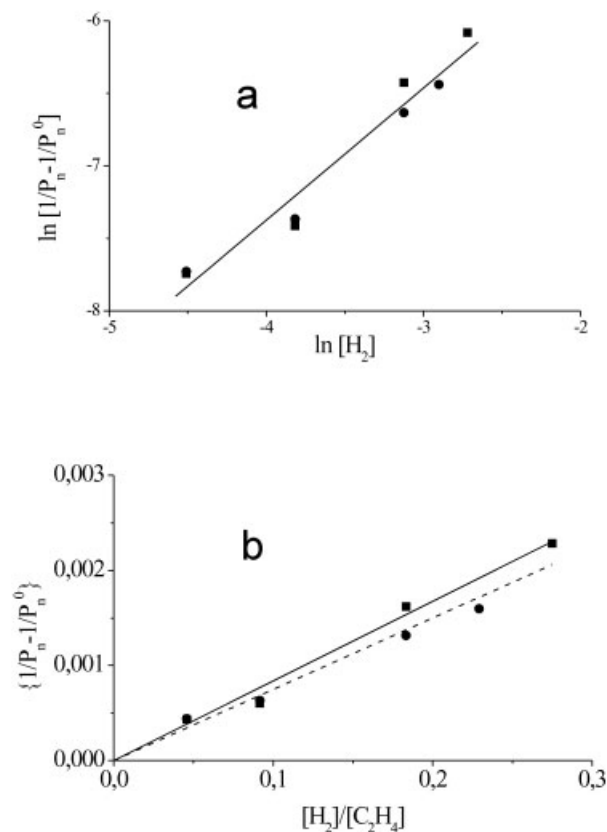


Figure 5 Plot for calculating the order of the chain transfer reaction with hydrogen (a) and K_{tr}^H/K_p values (b) for ethylene polymerization over TMC-0.07 (●) and TMC-5 (■).

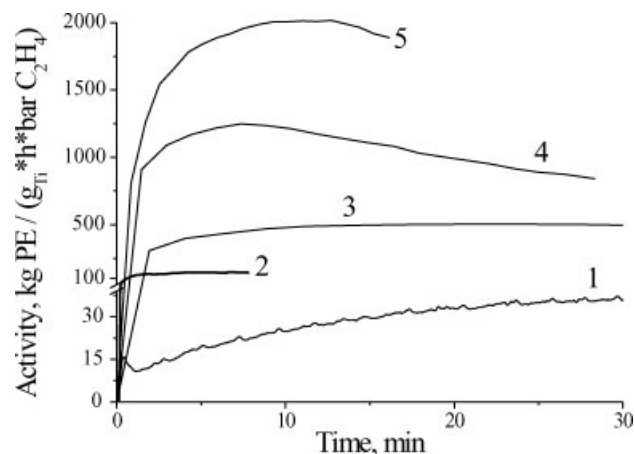


Figure 6 Kinetic profile of ethylene homopolymerization and copolymerization with hexene-1 over TMC-5 (curves 1 and 2) and TMC-0.07 (curves 3, 4, and 5): curves 1 and 3: homopolymerization with hydrogen at $[H_2]/[C_2H_4] = 0.125$; curves 2 and 4: copolymerization at $[C_6H_{12}]/[C_2H_4] = 2.6$, $[H_2]/[C_2H_4] = 0.125$; curve 5: copolymerization at $[C_6H_{12}]/[C_2H_4] = 2.6$, without hydrogen.

illustrates the effect of hydrogen concentration on P_n values of PE [logarithmic form of eq. (1)]. From these data, we determined the order of the reaction of chain transfer with hydrogen (n) and found the n value close to 1 (0.95) for both the catalysts studied. Then we plotted the dependence of $\{1/P_n - 1/P_n^0\}$ on $[H_2]/[C_2]$ [Fig. 5(b)] and calculated the ratio K_{tr}^H/K_p according to eq. (1). The data indicate TMC-0.07 and TMC-5 catalysts have similar hydrogen responds: K_{tr}^H/K_p values are close and make $7.5 \times 10^{-3} \text{ L/mol} \times \text{s}$ and $8.4 \times 10^{-3} \text{ L/mol} \times \text{s}$ correspondingly.

However, it is worth mentioning that molecular weight of PE produced without hydrogen on catalysts with the different titanium content essentially differs and makes 1.8×10^6 and 2.8×10^6 for TMC-0.07 and TMC-5, correspondingly (Table II, Experiments 1 and 6). One can propose, the rate of chain transfer reactions with monomer and organoaluminium co-catalyst for catalyst TMC-0.07 is higher when compared with that for TMC-5 catalyst. Probably, that is the reason for variety of MW values of PE produced with the same hydrogen concentration on TMC with different titanium content.

Ethylene-hexene-1 copolymerization over TMC with different titanium content

Taking into account the difference in activity of TMC with different titanium content and molecular weight characteristics of PE produced, we have investigated the ethylene-hexene-1 copolymerization over TMC-0.07 and TMC-5 catalysts. Experiments have been carried out at different hexene-1/ethylene molar ratio

($C_6H_{12}/C_2H_4 = 1.2-5$). In all cases, the catalyst activity in copolymerization experiments was considerably higher than that in homopolymerization ones. The kinetic curves of ethylene polymerizations and ethylene-hexene-1 copolymerization at molar ratio $C_6H_{12}/C_2H_4 = 2.6$, when the maximal activity of catalysts was achieved, are shown in Figure 6. One can see that the introducing of hexene-1 leads to sharp increase of the activity of catalysts with different titanium content. So, TMC-0.07 and TMC-5 demonstrate a three to four times increase of activity at ethylene-hexene-1 copolymerization ($C_6H_{12}/C_2H_4 = 2.6$) (Fig. 6). Generally, the activity of TMC-0.07 is ten times higher than that of TMC-5 catalyst both at ethylene homopolymerization and at ethylene-hexene-1 copolymerization.

The maximum of TMC activity was registered at ethylene-hexene-1 copolymerization without hydrogen on TMC-0.07 catalyst. This value reaches 2000 kg PE/(gTi \times h \times bar C_2H_4) or 96 kg PE/(mmolTi \times h \times bar C_2H_4) (Fig. 6, curve 5). The registered value of activity is extremely high and compares well with the activity of homogeneous metallocene and postmetallocene catalysts, which are known as the most active ones.

It is known that, in comparison with ethylene homopolymerization, the substantial increase of activity is observed at ethylene- α -olefins copolymerization over catalysts of different composition (the so-called co-monomer effect).¹²⁻¹⁶ The reasons for this phenomenon have not been explained unambiguously and are still being discussed in the literature.

We have determined co-monomer reactivity ratios (r_1 values) at ethylene-hexene-1 copolymerization on TMC-0.07 and TMC-5. Experimental data on co-monomer concentration ratio in polymerization medium $[C_6H_{12}]/[C_2H_4]$ and in copolymer $(C_6H_{12}/C_2H_4)_{pol}$ were treated in accordance with the simplified equation of copolymerization.¹⁵⁻¹⁷

$$(C_6H_{12}/C_2H_4)_{pol} = 1/r_1 [C_6H_{12}]/[C_2H_4] \quad (3)$$

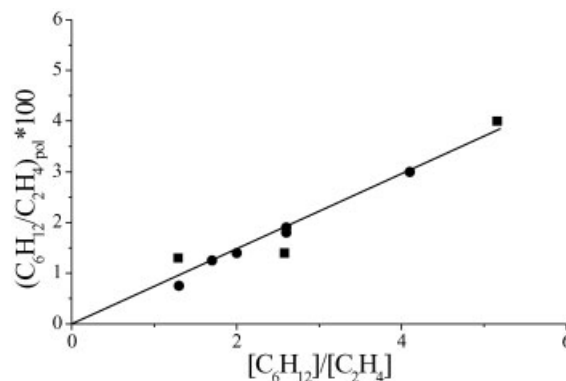


Figure 7 Co-monomer mole ratio in copolymer versus co-monomer mole ratio in heptane for TMC-0.07 (●) and TMC-5 (■).

The results of these calculations are given in Figure 7. It is shown that TMC with different titanium content possess a close copolymerizing ability: r_1 values are the same for TMC-0.07 and TMC-5 and make $r_1 = 135$.

Certainly, it should be kept in mind that r_1 as well as K_p and K_{tr}^H are the averaged values and characterize a set of active centers different in reactivity for the multisite catalysts like TMC. Nevertheless, the similarity of r_1 values as well as K_p and K_{tr}^H values (aforementioned) for TMC with different titanium content confirms the conclusion that the great difference in activity of these catalysts is mainly caused by the difference in the number of active centers.

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