ORIGINAL PAPER

The influence of magnesium dichloride as support on molecular weights of the polyethylenes produced by Ziegler-Natta catalyst

Tatiana B. Mikenas*, Alexander V. Shloma, Vladimir A. Zakharov*, Mikhail A. Matsko

Boreskov Institute of Catalysis SB RAS, pr. Akademika Lavrentieva, 5, 630090 Novosibirsk, Russia

ABSTRACT

The paper presents data on the effect exerted by magnesium dichloride in Ziegler-Natta catalysts on the activity and molecular weight of polyethylene (PE) produced by ethylene polymerization in the absence or presence of hydrogen. It was found that ethylene polymerization in the absence of hydrogen over titanium-magnesium catalysts (TMCs) with different ratio of titanium chloride and magnesium dichloride (Ti/Mg = 0.5 and 0.07), oxidation state of titanium ($TiCl_3$ or $TiCl_4$) and structural characteristics of the catalysts leads to the formation of PE with a close molecular weight. At the same time, PE obtained over a δ-$TiCl_3$ catalyst has a much (threefold) higher molecular weight. The introduction of hydrogen during polymerization for decreasing the molecular weight of PE is accompanied by a sharp drop in activity of the δ-$TiCl_3$ catalyst, in distinction to the highly active supported TMC containing 3 wt. % Ti. Data about the effect of hydrogen content during polymerization on the molecular weight of PE were used to calculate the ratio of rate constants for polymer chain transfer with hydrogen (K_{tr}^H) and polymer chain propagation reaction (K_p). This value was close for TMCs of different composition containing magnesium dichloride. In the case of δ-$TiCl_3$, the K_{tr}^H/K_p value was approximately two times lower compared to TMCs. **Polyolefins J (2024) 11: 235-242**

Keywords: Ziegler-Natta catalysts; magnesium dichloride; titanium-magnesium catalysts composition and structure; ethylene polymerization; molecular weight characteristics of polyethylene.

INTRODUCTION

Supported Ziegler-type catalysts with the composition $TiCl_4/MgCl_2+AlR_3$ are widely used in large-tonnage production of polyolefins. More than 50% of different grades of high density polyethylene (HDPE) and linear low density PE (LLDPE) are obtained over titanium-magnesium catalysts (TMCs) [1-5].

The elucidation of relations between composition and structure of advanced Ziegler-Natta catalysts and molecular weight characteristics of polyethylene and copolymers of ethylene with α-olefins produced over these catalysts is an important fundamental and applied problem.

The "activated" magnesium chloride (δ-$MgCl_2$) support with a high specific surface area and disordered crystal structure is the main component of advanced supported Ti-Mg catalysts. The main function of $MgCl_2$ in TMCs is to enhance the activity of a Ziegler-type catalyst by increasing the number of active sites [6-10], and to form the polymer particles with the specified morphology [11-14]. The literature provides limited

*Corresponding Author - E-mail: mikenas@catalysis.ru
zva@catalysis.ru

The influence of magnesium dichloride as support on molecular weights of the polyethylenes produced by Ziegler-Natta catalyst

IPPI

data concerning the effect of magnesium chloride in TMC on the molecular weight of produced PE. Earlier it was noted that TMCs produce PE with a lower medium-viscosity molecular weight (M_v) compared to the polymer obtained over a conventional Ziegler-Natta catalyst ($TiCl_3$) [9]. However, the literature provides no data on the effect exerted by this support on the molecular weight characteristics of the produced polyethylene and sensitivity of Ziegler-Natta catalysts to hydrogen as a polymer chain transfer agent.

In this work, we studied the effect of magnesium dichloride as a component of Ziegler-Natta catalysts on their activity in ethylene polymerization and molecular weight characteristics of polyethylene obtained in the absence and presence of hydrogen. Two variants of titanium-magnesium catalysts were used in the study: TMC-M containing $TiCl_3$ as the active component at the ratio $MgCl_2/TiCl_3 = 2$, and TMC containing $TiCl_4$ anchored on the δ-$MgCl_2$ support with the composition $0.07TiCl_4/MgCl_2$. The δ-$TiCl_3$ sample has been used as a Ziegler-Natta catalyst not containing magnesium dichloride.

EXPERIMENTAL

Synthesis of supports and catalysts

Synthesis of nonsolvated solid butylmagnesium chloride (BuMgCl)
Solid non-solvated BuMgCl was obtained by reacting metallic powdered magnesium with *n*-butyl chloride in heptane. A 0.5 L dry glass reactor purged with argon was loaded with 4.8 g magnesium and 0.1 g iodine; after heating the reactor to 75°C, 1.5 ml n-butyl chloride was introduced. Upon initiation, the reaction mixture was cooled to 50°C and 100 ml of *n*-heptane was added; 19.4 ml of n-butyl chloride in 100 ml of heptane (*n*-BuCl/Mg = 1.0 (mol)) was introduced at 68-70°C for 2.5 hours. After that, the mixture was held at 70°C for 1 hour. A suspension of the obtained product (solid butyl magnesium chloride) was cooled to room temperature and used to synthesize S-1 support and TMC-M catalyst.

Synthesis of S-1 support
The S-1 support was obtained by the chlorination of solid butylmagnesium chloride with phenyltrichlorosilane ($PhSiCl_3$). A BuMgCl suspension in heptane was loaded in the glass thermostatted reactor equipped with a magnetic stirrer. $PhSiCl_3$ was uniformly added to the mixture ($PhSiCl_3$:BuMgCl = 3:1 (mol)) for an hour

at 60°C. The mixture was then held at a temperature of 90°C for an hour. After that, the mother liquor was removed from the reactor and the support was washed with heptane three times at 50°C. The support contained 20 wt.% magnesium and 1.1 wt.% Si.

Synthesis of TMC-M catalyst
The TMC-M catalyst was synthesized by interacting the BuMgCl suspension in heptane with $TiCl_4$. A $TiCl_4$ solution in heptane was added to the suspension of BuMgCl in heptane (BuMgCl:$TiCl_4$ = 1:1 (mol)) at 55°C for an hour. The mixture was held at 60°C for an hour. The mother liquor was removed from the reactor and the obtained catalyst was washed with heptane at 50°C. The catalyst had the composition $TiCl_3 \cdot 2MgCl_2$.

Synthesis of TMC-1 catalyst
The TMC-1 catalyst was synthesized by treating the support (S-1) with titanium tetrachloride (the molar ratio Ti/Mg = 1) at 60°C for an hour. The resulting catalyst was washed with heptane at 50°C. TMC-1 catalyst contained 3 wt.% titanium, 21 wt.% magnesium and 0.55 wt.% Si.

Polymerization
Polymerization was carried out in a 1 L stainless steel reactor at ethylene pressure 0.4 MPa, with $AlEt_3$ as cocatalyst (1.3 mmol L^{-1}), temperature 80°C, heptane as a solvent, for 1 hour. Content of hydrogen at polymerization is noted in Table 3 and Figs. 3 and 4.

Measurements
The titanium and magnesium concentrations in the catalyst were measured by AES-ICP on an Optima 5300 DV spectrometer.

MWD measurements of polymers prepared in the presence of hydrogen were carried out using a high-temperature gel permeation chromatography (GPC) PL 220 system in 1,2,4-trichlorobenzene at temperature of 160°C.

Intrinsic viscosity of high molecular weight polyethylene prepared in the absence of hydrogen was estimated according to ISO 1628. The obtained intrinsic viscosity of polyethylene was used to calculate the average molecular weight by the Margolies equation (1):

$$M_v = 5.37 \times 10^4 \eta^{1.49} \tag{1}$$

where M_v is the average molecular weight, g/mol; and η is the intrinsic viscosity, dL/g

X-ray diffraction analysis (XRD) of the samples was carried out on a Bruker D8 diffractometer using a Cu Kα source (λ = 1.54184 Å).

The average particle size (D^{50}) of the supports and catalysts were determined on a Mastersizer 2000 instrument.

The specific surface area and pore structure of the samples were analyzed using low-temperature nitrogen adsorption on a Autosorb-6B-Kr instrument. ESR spectra of the samples were recorded at a temperature of 77 K on a Bruker ER200D spectrometer.

RESULTS AND DISCUSSION

Composition and structure of the supports and catalysts

Table 1 lists data on the composition, specific surface area and particle size of the magnesium-containing presupport (butylmagnesium chloride), support, and titanium-magnesium catalysts synthesized using the indicated supports (exps. 1 and 2, 3 and 4), as well as the Ziegler-Natta catalyst sample (δ-TiCl$_4$, exp. 5).

The titanium-magnesium catalyst TMC-M (exp. 2, Table 1) was synthesized by the interaction of a solid magnesium-containing presupport with the composition MgBu$_2$•MgCl$_2$ (exp. 1, Table 1) and titanium tetrachloride. In this case, the catalyst is formed via the interaction of TiCl$_4$ with magnesium dibutyl in the MgBu$_2$•MgCl$_2$ presupport to form titanium trichloride in a combination with magnesium dichloride at the molar ratio MgCl$_2$/TiCl$_3$ $\cong$ 2.

Evidently, a considerable part of titanium trichloride in this sample resides in the bulk of the catalyst particles, similar to the δ-TiCl$_3$ catalyst containing 23.5 wt.% Ti (exp. 5, Table 1).

The ESR data obtained for TMC-M and δ-TiCl$_3$ catalysts (exps. 2 and 5, Table 1) are illustrated in Figure 1.

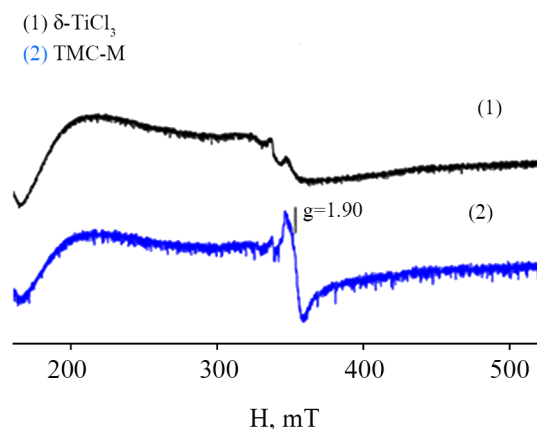The ESR spectrum of the δ-TiCl$_3$ catalyst contains

Figure 1. ESR spectra (77 K) for samples δ-TiCl$_3$ (spectrum 1) and TMC-M catalyst with the composition TiCl$_3$•2MgCl$_2$ (spectrum 2).

virtually no signals of Ti^{3+} ions in the region of q = 1.8 - 2.0 (Figure 1, spectrum 1), which are usually observed in supported titanium-magnesium catalysts with the composition TiCl$_4$/MgCl$_2$ after their interaction with aluminum trialkyl [15, 16]. These signals are attributed to isolated mononuclear Ti^{3+} compounds formed on the surface of δ-MgCl$_2$ support [16]. At the same time, a signal with q = 1.9 is observed in the ESR spectrum of TMC-M catalyst with the composition TiCl$_3$•2MgCl$_2$ (Figure 1, spectrum 2), which corresponds to Ti^{3+} ions. The intensity of this signal indicates that the sample contains paramagnetic Ti^{3+} ions in the amount of 5.1 ± 0.1 µmol/g cat, which constitutes 3.4 % of the total titanium content in the TMC-M catalyst. This result testifies that the presence of magnesium dichloride in TMC-M catalyst with the composition TiCl$_3$•2MgCl$_2$ leads to the formation of isolated mononuclear TiCl$_3$ compounds due to the presence of MgCl$_2$ in the second coordination sphere for a part of Ti^{3+} ions in this catalyst.

The δ-MgCl$_2$ support (exp. 3, Table 1) was obtained by the interaction of solid magnesium-containing presupport with the composition MgBu$_2$•MgCl$_2$ (exp. 1, Table 1) with phenyltrichlorosilane. This support

Table 1. Data on the composition, average particle size and surface area of supports and catalysts.

Exp. No.	Sample	Composition of samples			D_{50} (1) µm	S_{BET} m²/g	Oxidation state of titanium in the catalyst
		Ti, wt.%	Mg, wt.%	Composition			
1	Presupport "BuMgCl"	—	21.9	MgBu$_2$•MgCl$_2$	—	—	—
2	Catalyst TMC-M	12.4	11.5	TiCl$_3$•2MgCl$_2$	16.2	136	Ti^{3+}
3	Support δ-MgCl$_2$	—	20.0	MgCl$_2$(Si)(2)	13.8	129	—
4	Catalyst TMC-1	3.0	21.0	0.07TiCl$_4$•MgCl$_2$ (Si)(3)	10.4	183	Ti^{4+}
5	Catalyst δ-TiCl$_3$	23.5	—	δ-TiCl$_3$	12.5	162	Ti^{3+}

(1)Average particle size. (2) Content of Si, 1.1 wt.%. (3) Content of Si, 0.55 wt.%.

The influence of magnesium dichloride as support on molecular weights of the polyethylenes produced by Ziegler-Natta catalyst
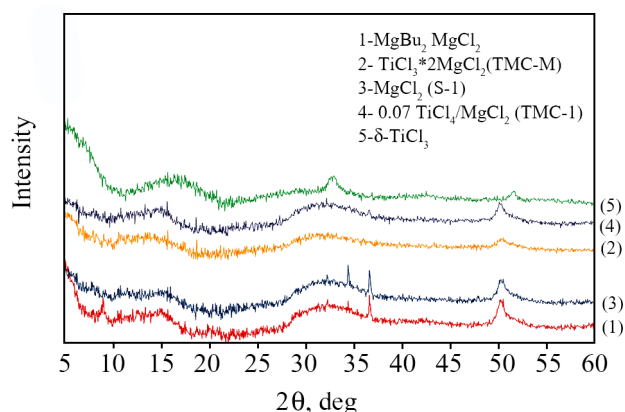
IPPI

Figure 2. Diffraction patterns of support and catalyst samples listed in Table 1 (the numbers of diffraction patterns correspond to the numbers in Table 1).

has quite a high specific surface area (129 m^2/g) and contains a minor amount of silicon compounds (1.1 wt.% Si). The supported titanium-magnesium catalyst TMC-1, which was obtained by the treatment of this support with titanium tetrachloride, has a high specific surface area (183 m^2/g) and contains 3.0 wt.% Ti in the form of $TiCl_4$ compounds anchored on the δ-MgCl$_2$ surface.

The crystal structure of the support and catalyst samples listed in Table 1 was examined by XRD. Figure 2 displays diffraction patterns of these samples.

One can see that the diffraction patterns of all the magnesium-containing samples, particularly the MgBu$_2$·MgCl$_2$ presupport (exp. 1, Table 1), contain 2θ diffraction peaks in the region of 15°, 29-35° and 50°, which characterize the layered structure of MgCl$_2$. The presence of a broad halo in the region of 2θ = 29-35° indicates the turbostratic disorder of Cl-Mg-Cl layers in these samples, which is typical of the activated δ-MgCl$_2$ [11]. The diffraction pattern of the δ-TiCl$_3$ sample (sample 5 in Figure 2) also testifies to the disordered layered structure of this sample, as a result of which a part of reflections in the region of 2θ

Table 2. X-ray data on the interlayer distance and crystallite size of δ-MgCl$_2$ in the supports and catalyst samples listed in Table 1.

No.	Composition of samples	d$_{003}$[1] A^0	<D$_{001}$>[2] nm	<D$_{110}$>[3] nm
1	MgBu$_2$•MgCl$_2$	6.2	2.1	12.0
2	Catalyst TMC-M TiCl$_3$•2MgCl$_2$	6.4	1.3	11.2
3	Support δ-MgCl$_2$	5.9	3.9	10.4
4	Catalyst TMC-1	6.0	3.2	10.0

[1]Interlayer distance.
[2]Average crystallite size perpendicular to Cl-Mg-Cl layers.
[3]Average crystallite size along Cl-Mg-Cl layers.

= 29-35° does not show up.

Table 2 lists data on the interlayer distances and microcrystallite sizes calculated from the diffraction patterns shown in Figure 2. For all the samples of microcrystallites, the size along magnesium dichloride layers <D110> is in the range from 10 to 12 nm. The size of microcrystallites perpendicular to magnesium dichloride layers <D001> is much smaller, being equal to 1.3 nm for sample (2) and 3.9 nm for sample (3). The size of microcrystallites in this direction decreases from 2.1 to 1.3 nm (samples 1 and 2) and from 3.9 to 3.2 nm (samples 3 and 4) upon interaction of supports (samples 1 and 3) with TiCl$_4$ leading to the formation of titanium-magnesium catalysts (samples 2 and 4). Note that the 1.3 nm value for TMC-M catalyst (sample 3) corresponds to the presence of three Cl-Mg-Cl layers in the crystallites of this catalyst, while the 3.2 nm value corresponds to the presence of seven Cl-Mg-Cl layers in the crystallites of TMC-1 catalyst. The greater size of crystallites in the δ-MgCl$_2$ support (sample 3, Table 2) along the 001 direction ensures a larger surface fraction of the lateral faces of MgCl$_2$ crystallites with respect to the total surface of the crystallites. Accordingly, this allows increasing the amount of TiCl$_4$ anchored on the δ-MgCl$_2$ surface due to the interaction with fourfold and fivefold coordinated magnesium ions residing on the lateral faces of δ-MgCl$_2$ crystallites.

Ethylene polymerization over TMC-M, TMC-1 and δ-TiCl$_3$ catalysts and data on the molecular weight characteristics of produced polyethylene
Data on the activity of catalysts with different composition during ethylene polymerization in the absence or presence of hydrogen, molecular weight and polydispersity (M$_w$/M$_n$ values) of the produced polyethylene are presented in Table 3 and Figure 3.

Activity of the catalysts increases in passing from the Ziegler-Natta catalyst δ-TiCl$_3$ to titanium-magnesium catalysts TMC-M and TMC-1 (exps. 1, 5 and 9, Table 3). Most pronounced (by a factor of 4-16) is an increase in the activity per unit weight of titanium (kg/g Ti). The introduction of hydrogen as a polymer chain transfer agent leads to a substantial decrease in activity during polymerization over δ-TiCl$_3$ and TMC-M catalysts. At the same time, in the case of polymerization over supported TMC-1 catalyst, only a minor decrease in activity upon hydrogen introduction is observed (Figure 3). As a result, the activity of TMC-1 catalyst (kg/g Ti) during polymerization in the presence of hydrogen increases 35-fold in comparison with

Table 3. Data on the activity of catalysts with different composition during ethylene polymerization, molecular weight of polyethylene produced, and effect of hydrogen on the molecular weight and molecular weight distribution of polyethylene.

Catalyst[1]	Exp. No.	P_{H2}, bar	PE yield[2]		M_w, kg/mol	M_n, kg/mol	M_w/M_n
			kg/g cat	kg/g Ti			
(5) δ-TiCl₃	1	—	2.9	12.3	5900[3]	—	—
	2	1	1.5	6.4	600	120	5.0
	3	2	1.2	5.1	387	82	4.7
	4	4	1.0	4.3	240	46	5.2
(2) TMC-M (TiCl₃•2MgCl₂)	5	—	6.5	52.4	1900[3]	—	—
	6	1	3.9	31.5	266	59	4.5
	7	2	3.3	26.6	180	35	5.2
	8	3	3.1	25.0	140	27	5.2
(4) TMC-1 (0.07TiCl₄•MgCl₂)	9	—	5.7	190	2044[3]	—	—
	10	1	5.6	187	200	51	3.9
	11	2	5.4	180	140	35	4.0
	12	4	4.9	163	87	20	4.4

[1] Catalyst numbers and data on the catalyst composition are listed in Table 1.
[2] Polymerization at 80°C, ethylene pressure 4 bar, for 1 hour.
[3] M_v values calculated from data on the intrinsic viscosity of PE samples.

δ-TiCl₃ catalyst (exps. 3 and 11, Table 3). As shown in [17], a decrease in activity of titanium-magnesium catalysts upon hydrogen introduction is the reversible process associated with the reversible adsorption of dialkylaluminum hydride, which is formed in the reaction medium in the presence of hydrogen on the active sites or their precursors in titanium-magnesium catalysts.

Table 3 lists also data on the molecular weight and polydispersity (M_w/M_n values) of the polymers obtained during ethylene polymerization over catalysts with different composition in the presence and absence of hydrogen. The medium-viscosity molecular weight of polyethylene produced in the absence of hydrogen (the M_v value) has a very high value for each of the three catalysts. One can see that this value sharply decreases in passing from the δ-TiCl₃ catalyst (exp. 1, Table 3, M_v = 5900 kg/mol) to titanium-magnesium catalysts TMC-M and TMC-1 (exps. 5 and 9, Table 3, M_v = 1900-2044 kg/mol). Note that the content of titanium in these catalysts (the Ti/Mg ratio) and the oxidation state of titanium chloride (TiCl₃ in the case of TMC-M and TiCl₄ in the case of TMC-1) exert virtually no effect on the M_v value.

The introduction of hydrogen during polymerization leads to a sharp decrease in the molecular weight of produced polyethylene for all three catalysts. Therewith, molecular weights of the polymers obtained over titanium-magnesium catalysts TMC-M and TMC-1 at the same hydrogen content have close values. It should be noted that the polymers formed over the supported catalyst TMC-1 (exps. 10-12, Table 3) have a slightly narrower molecular weight distribution

(M_w/M_n = 3.9-4.4) compared to the polymers produced over TMC-M catalyst (M_w/M_n = 4.5-5.2, exps. 6-8, Table 3). This may result in slight differences in the molecular weight of polymers obtained over these catalysts at a similar hydrogen content (for example, in exps. 6 and 10, Table 3). At the same time, it is seen that polydispersity of the polymers formed over TMC-M is close to that of polyethylene produced over δ-TiCl₃. On both catalysts, polymers with M_w/M_n = 4.5-5.2 (exps. 2-4 and 6-8, Table 3) are formed.

Data of Table 3 show that at a quite high content of hydrogen in the reaction medium (20-50 % of hydrogen in the reactor gas phase) a sharp (by a factor of 10-24) decrease in the molecular weight of produced polyethylene is observed for all the catalysts in comparison with the experiments without hydrogen. This result demonstrates that under the indicated conditions the polymer chain
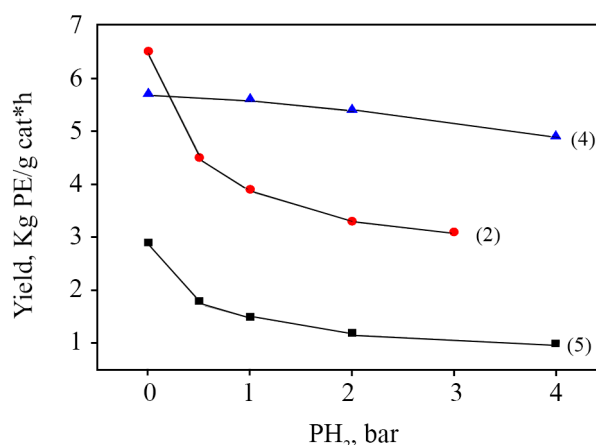

Figure 3. Data on the effect of hydrogen content on the activity of catalysts listed in Table 3 (catalyst δ-TiCl₃ (5) - ■ -, catalyst TMC-M (2) - • -, catalyst TMC-1 (4) - ▲ -).
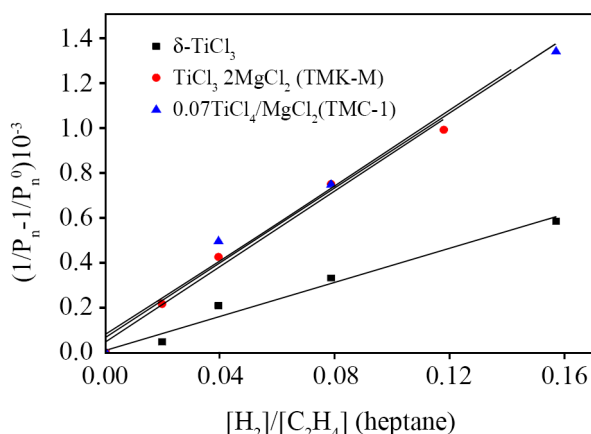
The influence of magnesium dichloride as support on molecular weights of the polyethylenes produced by Ziegler-Natta catalyst

IPPI

Figure 4. Dependences of the $(1/P_n – 1/P_n^0)$ values on the $[H2]/[C_2H_4]$ ratios in heptane obtained during polymerization of ethylene on various Ti-containing Ziegler-type catalysts (polymerization conditions in Table 3).

transfer with hydrogen is the predominant transfer reaction. The results of experiments 2-4, 6-8 and 10-12 (Table 3) can be used to calculate the ratio of reaction rate constants for chain transfer with hydrogen (K_{tr}^H) and polymer chain propagation (K_p) using the known equation (2) [18, 19-21]:

$$\frac{1}{\overline{P}_n} - \frac{1}{\overline{P}_n^0} = \frac{k_{tr}^H \times [H_2]}{k_p \times [C_2H_4]} \qquad (2)$$

where $\overline{P}_n$ is the number-average degree of polymerization; and $\overline{P}_n^0$ is the number-average degree of polymerization in the experiment without hydrogen. The linear dependence of $(1/P_n-1/P_n^0)$ vs. $[H_2]/[C_2H_4]$, which was plotted using the M_n values for exps. 2-4, 6-8 and 9-12 in Table 3, is displayed in Figure 4. These data were used to calculate the K_{tr}^H/K_p values, which were found to be close for TMCs of different composition ($9\cdot10^{-3}$). In the case of δ-TiCl$_3$, the K_{tr}^H/K_p ratio was approximately two times lower than for TMCs ($3.9\cdot10^{-3}$).

The data obtained demonstrate that the introduction of MgCl$_2$ in the Ziegler-type catalyst enhances its efficiency in controlling the molecular weight of polyethylene by hydrogen.

CONCLUSION

Data on the composition and structure of two variants of titanium-magnesium catalysts with different content of magnesium dichloride and titanium chloride were acquired: (1) the TMC-M catalyst containing titanium trichloride at the molar ratio MgCl$_2$/TiCl$_3$ = 2, and

(2) the TMC-1 catalyst containing TiCl$_4$ anchored on the δ-MgCl$_2$ support at the molar ratio TiCl$_4$/MgCl$_2$ = 0.07. Both catalysts have close sizes of δ-MgCl$_2$ microcrystallites (10-11 nm) along Cl-Mg-Cl layers, but considerably differ in the size of microcrystallites perpendicular to Cl-Mg-Cl layers (1.3 nm for TMC-M and 3.2 nm for TMC-1).

The δ-TiCl$_3$ catalyst does not contain mononuclear Ti^{3+} compounds that can be identified by ESR. Meanwhile, such compounds are observed in the ESR spectrum of TiCl$_3$·2MgCl$_2$ catalyst (TMC-M). However, their amount is not large and constitutes only 3.4 % of the total titanium content in this catalyst.

The activity of titanium-magnesium catalysts during ethylene polymerization calculated per unit weight of titanium strongly exceeds the activity of δ-TiCl$_3$ catalyst. Therewith, the maximum activity (190 kg/g Ti) is observed for the TMC-1 catalyst, which contains TiCl$_4$ compounds anchored on the surface of δ-MgCl$_2$ support. It should be noted that the activity of δ-TiCl$_3$ and TiCl$_3$·2MgCl$_2$ catalysts, in distinction to TMC-1 catalyst, decreases considerably upon polymerization in the presence of hydrogen as the chain transfer agent, and the difference in activity of TMC-1 and δ-TiCl$_3$ catalysts during polymerization in the presence of hydrogen becomes even more pronounced.

Ethylene polymerization over δ-TiCl$_3$ catalyst in the absence of hydrogen leads to the formation of polyethylene with a super-high molecular weight (M_v=5900 kg/mol). The presence of MgCl$_2$ in the composition of TMC-M and TMC-1 catalysts produces a sharp decrease in the molecular weight of polyethylene to 1900-2040 kg/mol. Therewith, the molecular weight of polyethylene does not depend on the ratio of magnesium dichloride and titanium chloride or the oxidation state of titanium in the initial titanium-magnesium catalyst.

The introduction of hydrogen during polymerization leads to a sharp (by a factor of 10 – 24) decrease in the molecular weight of polyethylene obtained over all three catalysts depending on the hydrogen content. Therewith, polydispersity of the polymers produced over δ-TiCl$_3$ and TiCl$_3$·2MgCl$_2$ catalysts has close values (M_w/M_n = 4.5-5.2). Polymers formed over the supported catalyst TMC-1 have a narrower molecular weight distribution (M_w/M_n = 3.9-4.4).

Data about the effect of hydrogen content on the molecular weight of polyethylene were used to calculate the ratio of rate constants for chain transfer with hydrogen (K_{tr}^H) and polymer chain propagation (K_p) reactions. The obtained value is close for TMCs

of different composition and equal to $9 \cdot 10^{-3}$. In the case of δ-$TiCl_3$, the K_{tr}^H/K_p ratio is approximately two times lower compared to the value for TMCs ($3.9 \cdot 10^{-3}$).

ACKNOWLEDGEMENTS

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Spalding MA, Chatterjee AM (eds) (2017) Handbook of industrial polyethylene and technology: definitive guide to manufacturing, properties, processing, applications and markets. Scrivener Publishing LLC, Beverly, MA, USA
2. Paulik C, Spiegel G, Jeremic D (2019) Bimodal polyethylene: Controlling polymer properties by molecular design. In: Multimodal polymers with supported catalysts, Albunia AR, Prades F, Jeremic D (eds), Springer, Cham
3. Nowlin TE (2014) Business and technology of the global polyethylene industry: An in-depth look at the history, technology, catalysts, and modern commercial manufacture of polyethylene and its products, Wiley-Scrivener Publishing, Salem, MA, USA
4. Sauter DW, Taoufik M, Boisson C (2017) Polyolefins, a success story. Polymers 9: 185
5. Plastics Europe: Plastics-The Facts (2020) Available online: https://plasticseurope.org/de/wp content/uploads/sites/3/2021/11/Plastics_the_facts-WEB-2020 version Jun21_final.pdf. Accessed 27 June 2022
6. Zakharov VA, Chumayevskii NB, Makhtarulin SI, Bukatov GD, Yermakov YI (1975) Determination of the number of propagation centers and the propagation rate constant for ethylene polymerization on supported titanium catalysts. React Kinet Catal Lett 2: 329-335
7. Zakharov VA, Bukatov GD, Chumayevskii NB, Yermakov YI (1977) Study of the mechanism of propagation and transfer reactions in the polymerization of olefins by Ziegler-Natta catalysts, 4. The kinetic scheme for propagation and chain transfer reactions. Macromol Chem 178: 967-980
8. Zakharov VA, Bukatov GD, Yermakov YI (1983) On the mechanism of olefin polymerization by Ziegler-Natta catalysts. Industrial Developments. Adv Polym Sci 51: 61-100
9. Zakharov VA, Bukatova ZK, Makhtarulin SI, Chumaevsky NB, Ermakov YI (1979) Chain transfer in polymerization of ethylene by highly active titanium-magnesium catalysts. Polym Sci 21: 544-550
10. Bukatov GD, Zakharov VA, Barabanov AA (2005) Mechanism of olefin polymerization on supported Ziegler-Natta catalysts based on data on the number of active centers and propagation rate constants. Kinet Catal 46: 166-176
11. Mikenas TB, Koshevoy EI, Cherepanova SV, Zakharov VA (2016) Study of the Composition and Morphology of New Modifications of Titanium-Magnesium Catalysts with Improved Properties in Ethylene Polymerization. J Polym Sci Pol Chem 54: 2545-2558
12. Mikenas TB, Koshevoy EI, Zakharov VA (2017) Effect of the structure of titanium–magnesium catalysts on the morphology of polyethylene produced. J Polym Sci Pol Chem 55: 2298-2308
13. Shams A, Mehdizadeh M, Teimoury H-R, Emami M, Mirmohammadi SA, Sadjadi S, Bardají E, Poater A, Bahri-Laleh N (2022) Effect of the Pore Architecture of Ziegler-Natta Catalyst on Its Behavior in Propylene/1-Hexene Copolymerization. J Ind Eng Chem 116: 359-370
14. Masoori M, Rashedi R, Sepahi A, Jandaghian MH, Nikzinat E, Houshmandmoayed S (2022) Structure-Performance Relationship (SPR) of Ziegler Natta catalysts ($TiCl_4/MgCl_2$-based) in ethylene/1-butene and ethylene/1-hexene copolymerization. J Polym Res 29: 317
15. Zakharov VA, Makhtarulin SI, Poluboyarov VA, Anufrienko VF (1984) Study of the state of titanium ions and the composition of the active component in titanium-magnesium catalysts for

The influence of magnesium dichloride as support on molecular weights of the polyethylenes produced by Ziegler-Natta catalyst

IPPI

ethylene polymerization. Macromol Chem 185: 1781-1793

16. Mikenas TB, Koshevoy EI, Zakharov VA, Nikolaeva MI (2014) Formation of isolated titanium (II) ions as active sites of supported titanium-magnesium catalyst for polymerization of olefins in supported Ziegler-Natta. Macromol Chem Phys 215: 1707-1720

17. Sukulova VV, Barabanov AA, Mikenas TB, Matsko MA, Zakharov VA (2018) Effect of hydrogen on the number of active centers and the propagation rate constant at ethylene polymerization over titanium-magnesium Ziegler-Natta catalysts. Mol Catal 445: 299-306

18. Natta G, Pasquon I (1959) The kinetics of the stereospecific polymerization of α-olefins. Adv Catal 11: 1-66

19. Echevskaya LG, Matsko MA, Mikenas TB, Nikitin VE, Zakharov VA (2006) Supported titanium–magnesium catalysts with different titanium content: Kinetic peculiarities at ethylene homopolymerization and copolymerization and molecular weight characteristics of polyethylene. J Appl Polym Sci 102: 5436-5442

20. Nikolaeva MI, Mikenas TB, Matsko MA, Echevskaya LG, Zakharov VA (2010) Heterogeneity of Active Sites of Ziegler-Natta Catalysts: The Effect of Catalyst Composition on the MWD of Polyethylene. J Appl Polym Sci 115: 2432-2439

21. Mikenas TB, Zakharov VA, Echevskaya LG, Matsko MA (2001) Ethylene Polymerization with Supported Vanadium-Magnesium Catalyst: Hydrogen Effect. Macromol Chem Phys 202: 75-481