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Titanium-magnesium catalysts for olefin polymerization — effect of titanium oxidation state on catalyst performance

Summary — In this work, we investigated the influence of oxidation state of titanium and the effect of ethoxy groups' introduction into titanium compounds on the catalytic properties of MgCl_2 — supported catalysts [with triisobutylaluminum (TIBA) or triethylaluminum (TEA) as cocatalyst] in ethylene polymerization and ethylene 1-hexene copolymerization, and on the polymer characteristics. To prepare supported titanium-magnesium catalysts of various compositions, soluble compounds of titanium in different oxidation states [η^6 -benzene- $\text{Ti}^{2+}\text{Al}_2\text{Cl}_8$, $\text{Ti}^{3+}\text{Cl}_3 \cdot n\text{DBE}$, and $\text{Ti}^{4+}(\text{OEt})_2\text{Cl}_2$] were synthesized, analyzed by ESR and ^{13}C NMR methods, and immobilized on the highly dispersed magnesium chloride. The data were obtained on the effects produced by composition and oxidation state of titanium compounds (covering also commonly used TiCl_4) on the activity, control of PE molecular weight by hydrogen, copolymerization ability, and molecular weight distribution (MWD) of polyethylene. The results obtained demonstrate that different titanium precursors comprising Ti(II), Ti(III) and Ti(IV) compounds supported on MgCl_2 allow preparing the highly active catalysts for ethylene polymerization or ethylene/1-hexene copolymerization. It was found that titanium oxidation state in the initial titanium compounds had a weak effect on the molecular weight and MWD of PE, whereas the ligand environment of titanium affected this parameter more strongly.

Key words: Ziegler-type catalysts, magnesium support, titanium oxidation states, polymerization, catalyst activity, polyethylene, molecular weight, molecular weight distribution.

TYTANOWO-MAGNEZOWE KATALIZATORY W POLIMERYZACJI OLEFIN — WPŁYW STOPNIA UTLENIEŃ ATOMU TYTANU NA WŁAŚCIWOŚCI KATALITYCZNE

Streszczenie — Otrzymano różniące się składem wysoce reaktywne tytanowo-magnezowe układy katalityczne obejmujące rozpuszczalne związki tytanu o różnym stopniu utlenienia [η^6 -benzeno- $\text{Ti}^{2+}\text{Al}_2\text{Cl}_8$, $\text{Ti}^{3+}\text{Cl}_3 \cdot n\text{DBE}$ (DBE = eter dibutyłowy) oraz $\text{Ti}^{4+}(\text{OEt})_2\text{Cl}_2$] i scharakteryzowano je metodami ESR a także ^{13}C NMR. Zbadano wpływ stopnia utlenienia tytanu oraz wprowadzenia do jego związków grup etoksyłowych na aktywność omawianych układów katalitycznych na nośniku MgCl_2 [z zastosowaniem triizobutyloglinu (TIBA) lub trietyloglinu (TEA) jako kokatalizatora] w polimeryzacji etylenu oraz jego kopolimeryzacji z 1-heksenem (tabela 1). W charakterze regulatora ciężaru cząsteczkowego produktów zastosowano wodór (tabele 2 i 3). Stwierdzono, że stopień utlenienia tytanu wywiera jedynie niewielki wpływ na wartości ciężaru cząsteczkowego (M_w) PE i jego rozkładu (MWD), podczas gdy rodzaj ligandu związanego z atomem tytanu zmienia te właściwości w istotny sposób. W kopolimeryzacji etylenu z 1-heksenem określono wartości współczynników reaktywności (r_1) etylenu wobec badanych katalizatorów (tabela 4).

Słowa kluczowe: katalizatory Zieglera-Natta, nośnik magnezowy, stopień utlenienia tytanu, polimeryzacja, aktywność katalizatora, polietylen, ciężar cząsteczkowy, rozkład ciężaru cząsteczkowego.

At present, polyolefins are commonly produced using a new generation of highly active supported titanium-magnesium Ziegler-Natta catalysts (TMC). Although TMC have been studied for many years, some aspects, such as the structure of active sites and interrelations between activity, polymer properties and valency of titanium in these catalysts, remain debatable [1—7]. In

particular, it is still unclear how the oxidation state and ligand environment of titanium affect the catalytic properties of TMC. Some authors [5, 6] related a broad molecular weight distribution (MWD) of polyethylene produced with TMC and the formation of various active sites containing Ti(II), Ti(III) and Ti(IV) compounds. Albizzati *et al.* [4] showed that the catalyst comprising a bivalent titanium compound of [η^6 -arene TiAl_2Cl_8] composition supported on magnesium chloride was highly

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active in propylene or ethylene polymerization; unfortunately, there are no data on the molecular structure of polymers produced.

In the present work, supported TMC have been synthesized using soluble compounds of Ti(II), Ti(III) and Ti(IV), titanium tetrachloride and titanium diethoxydichloride being among them. The data concerning the effects of titanium oxidation state and modification of titanium chloride by ethoxy groups on the catalytic activity in ethylene polymerization or ethylene/1-hexene copolymerization, and on the molecular weight characteristics of the polymers obtained were collected.

EXPERIMENTAL

Chemically pure TiCl_4 was used without additional purification.

Catalyst components and support

A divalent titanium complex $[\eta^6\text{-benzeneTiAl}_2\text{Cl}_8]$ was synthesized using Fisher-Hafner method [8] *via* TiCl_4 reduction by metal aluminum in the presence of AlCl_3 in a benzene medium. The resulting complex was transferred to a soluble state according to [9]: 1 g of solid titanium-benzene complex was dissolved in 100 g of benzene containing AlEt_3 at a concentration of 1 mmol/L for 2 h at 70 °C.

ESR spectra of the initial complexes are characterized by virtually total absence of trivalent titanium particles. Upon addition of excess water to a solution of $[\eta^6\text{-benzeneTiAl}_2\text{Cl}_8]$ complex, the Ti(II) to Ti(III) oxidation results in the appearance of an intense signal in the spectrum, which is typical for isolated paramagnetic ions of trivalent titanium.

A soluble $\text{TiCl}_3 \cdot n\text{DBE}$ (DBE = dibutyl ether) complex was synthesized according to [10] *via* the reduction of titanium tetrachloride by hydrogen at room temperature in 1,2-dichloroethane medium in the presence of carbon-supported palladium catalyst and DBE. The ESR spectrum of $\text{TiCl}_3 \cdot n\text{DBE}$ complex contains a signal assigned to Ti^{3+} ions. The concentration of isolated paramagnetic ions amounted to *ca.* 12 % of the total amount of titanium. After the addition of pyridine (Py/Ti = 50), which decomposes the associates of titanium compounds to form soluble adducts $\text{TiCl}_3 \cdot n\text{Py}$, an isotropic ESR signal of Ti^{3+} was observed ("Bruker ER200D" spectrometer), its intensity corresponding to the total content of titanium. Earlier this signal was observed in ESR spectra of supported TMC of $\text{TiCl}_4/\text{MgCl}_2$ composition after reduction by triethylaluminum followed by treatment with pyridine [11].

Titanium diethoxydichloride was obtained by mixing of equimolar amounts of TiCl_4 (5.5 ml) and $\text{Si}(\text{OEt})_4$ (11 ml) at room temperature in argon atmosphere for 2 h. After vacuum removal of a liquid compound $\text{Si}(\text{OEt})_2\text{Cl}_2$, the sediment of titanium ethoxychloride

was dissolved in toluene and identified by ^{13}C NMR spectroscopy ("Bruker AANCE 400" instrument, frequency 100.612 MHz, scan width 25 kHz, 90° pulse of 8 μs , accumulation frequency 0.1 Hz).

All the signals typical for ethoxy groups bonded to titanium are observed in the spectrum of a titanium ethoxychloride solution. The quantitative data derived from the ^{13}C NMR spectra were compared with the data of chemical analysis. The content of chlorine determined by potentiometric titration with silver nitrate was 28 %, which was close to a theoretical value (32 %) for $\text{Ti}(\text{OEt})_2\text{Cl}_2$.

A highly dispersed support MgCl_2 ($S_{\text{specif.}} \sim 190 \text{ m}^2/\text{g}$) was obtained according to [12] through the reaction of metal magnesium powder with an excess of butyl chloride in hydrocarbon solvent.

The catalysts were prepared by deposition of an excess or a calculated amount of titanium compound on magnesium-containing support in heptane at 20 °C. The reaction mixture was kept at 45–90 °C for 2 h, then an excess of titanium compound was removed by repeated washing with heptane.

The titanium contents in catalysts were determined by AES-ICP (*Atomic Emission Spectroscopy — Inductively Coupled Plasma*) using an "Optima 4300 DV" spectrometer.

The content of chlorine was found by potentiometric titration with silver nitrate.

The ESR spectra were taken in sealed molybdenum ampoules in X-range at temperatures 77 and 298 K at wavelength $\lambda = 3 \text{ nm}$.

The chemical shift in the ^{13}C NMR spectra was determined from the signal of toluene CH_3 group (20.4 ppm).

Ethylene polymerization and copolymerization

Ethylene slurry polymerization was performed in a 0.85 L steel reactor, in heptane, at constant ethylene pressure 0.4 MPa (4 bar) and temperature 80 °C for 1 hour. Organoaluminum compounds (OAC) — triisobutylaluminum (TIBA) or triethylaluminum (TEA) — were used as a cocatalyst, in concentration 5 mmol OAC/L, catalyst concentration was 0.02–0.04 g/L. Hydrogen (pressure 0.1 MPa = 1 bar) was used as a chain transfer agent to control molecular weight (M_w) of PE. In ethylene/1-hexene copolymerization, comonomer was introduced at the beginning of the experiment. Copolymer yield was limited in order to prevent the change of 1-hexene concentration over 15 wt. %.

Molecular weight characteristics of polymers (M_w , $M_w/M_n = MWD$) were determined by gel-permeation chromatography (GPC) using a "WATERS-150 C" instrument combined with a differential viscometer ("Viscotek Model 100"). Four TSK gel columns ("GMHXL-HT", Tosoh Corp.) were used in the study. The measurement conditions were as follows: 140 °C, 1,2,4-trichlorobenzene as a solvent, flow rate of 1 ml/min.

The content of CH₃ groups (absorption band at 1378 cm⁻¹) in a polymer was determined using an IR Fourier spectrometer "Shimadzu FTIR 8400S".

RESULTS AND DISCUSSION

Ethylene polymerization in the presence of TMC produced with titanium (II), (III) or (IV) chlorides and titanium diethoxydichlorides

TMC obtained by deposition of Ti(II), Ti(III) or Ti(IV) chlorides or titanium diethoxydichloride on a highly dispersed magnesium chloride (catalysts I, II, III and IV in Table 1) were tested in ethylene polymerization with two different cocatalysts (TIBA or TEA). Table 1 presents the data concerning the catalysts' activities and molecular weight characteristics of PE produced.

TMC activity

A distinctive feature of catalyst I containing divalent titanium is that it shows activity in ethylene polymerization (80 °C) in the absence of OAC [11 kg PE/(g Ti · h · atm C₂H₄)]. This result confirms that catalyst I actually contains a divalent titanium compound as the active

shown in [11] that catalysts TiCl₄/MgCl₂ and TiCl₃/MgCl₂, being free of ether, have similar activities. The lowest activity with TIBA as a cocatalyst was shown by catalyst IV prepared with titanium diethoxydichloride. This can be attributed to a lower reduction of titanium by triisobutylaluminum in this catalyst. As TEA is a stronger reducer than TIBA, the use of TEA as a cocatalyst leads to a 1.3–1.6-fold decrease in the activity of catalysts I, II and III containing titanium chlorides in different titanium oxidation states.

On the contrary, for catalyst IV containing titanium diethoxydichloride, the use of TEA instead of TIBA caused an increase in the activity *ca.* 3-fold. Activity of this catalyst reaches the activity of catalysts I and III containing titanium (II) and (IV) as the active components.

Molecular weight and MWD of PE

As it is seen from Table 1, catalysts I, II and III, containing titanium chlorides in different oxidation states, in the presence of cocatalyst TIBA let produce polyethylenes characterized with similar molecular weights (*M_w*) and *MWD* values. The introduction of ethoxy groups into titanium compound (catalyst IV) decreased molecular weight and gave narrower *MWD* values of PE

Table 1. Effect of titanium compound (Tiⁿ⁺, ligand) and AOC on the activity of catalyst (TMC) and PE properties

Titanium compound (denoting of catalyst)	[η ⁶ -BenzeneTiAl ₂ Cl ₈] (I)		TiCl ₃ · nDBE (II)		TiCl ₄ (III)		Ti(OEt) ₂ Cl ₂ (IV)	
Ti content, wt. %	0.7		1.0		0.9		0.4	
Cocatalyst	TEA	TIBA	TEA	TIBA	TEA	TIBA	TEA	TIBA
Activity of TMC, kg PE/(g Ti · h · atm C ₂ H ₄)	270	428	108	172	220	282	200	64
<i>M_w</i> · 10 ⁻⁴	28	31	22	28	22	28	18,5	24,5
<i>M_w</i> / <i>M_n</i>	4.5	5.2	5.4	4.7	4.4	4.7	4.1	3.6

component, since according to the literature data, divalent titanium compounds are active in ethylene polymerization without organoaluminum cocatalyst [13, 14]. Note that the mentioned activity of the supported catalyst obtained in our study (11 kg PE/g Ti · h · atm C₂H₄) is approximately two orders of magnitude higher as compared to the activity of bulk TiCl₂ (0.16 kg/g Ti · h · atm C₂H₄) [14]. The data in Table 1 show that in the case of TMC containing titanium chlorides in different oxidation states (catalysts I, II and III), TIBA used as co-catalyst with a lower reducing ability than TEA shows a higher activity. In this case, catalyst I containing 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 TiCl₃ · nDBE/MgCl₂ composition is less active as compared to conventional catalyst III of TiCl₄/MgCl₂ composition. This may be caused by partial blocking of DBE active sites. Previously, it was

for both TIBA or TEA cocatalysts used. When TIBA is replaced with TEA, the PE molecular weight decreases for all the TMC catalysts studied. This is due to the fact that TEA is a more efficient chain transfer agent as compared to TIBA. *MWD* of PE depends on the composition of cocatalyst for all the catalysts studied, but irregularly, contrary to *M_w* changes.

To estimate quantitatively the reactivity of TMC in the chain transfer reaction with hydrogen, catalysts I and IV containing titanium (II) chloride and titanium (IV) diethoxydichloride as the active components were studied in ethylene polymerization at a varying H₂/C₂H₄ ratio, and compared with the standard TMC of TiCl₄/MgCl₂ composition (catalyst III) (Table 2). The experimental data obtained were used to determine the order of chain transfer reaction with hydrogen and to calculate the ratio of the rate constant of chain transfer with hydrogen (*k_{tr}^H*) and the propagation rate constant (*k_p*) using the known relations [15, 16]. It was found that for all studied catalysts the order of chain transfer reac-

Table 2. Effect of hydrogen concentration on the activity of TMC, M_w and MWD of PE

Titanium compound (denoting of catalyst)	$[\eta^6\text{-BenzeneTiAl}_2\text{Cl}_8]^1$ (I)	TiCl_4^1 (III)	$\text{Ti}(\text{OEt})_2\text{Cl}_2^2$ (IV)
Ti content, wt. %	0.7	2.0	2.0
$[\text{H}_2]/[\text{C}_2\text{H}_4]$	0 0.25 0.5 1.0	0 0.25 0.5 1.0	0 0.25 0.5 1.0
Activity of TMC kg PE/(g Ti · h)	864 428 356 352	432 300 248 176	156 96 92 68
$M_w \cdot 10^{-4}$	300 ³⁾ 31 22 12	300 ³⁾ 33 19 12	130 ³⁾ 20 14 9
M_w/M_n	— 5.2 4.4 6.7	— 5.5 5.8 8.0	— 4.3 4.5 4.5

¹⁾ TIBA as cocatalyst. ²⁾ TEA as cocatalyst. ³⁾ Calculated from intrinsic viscosity ($M_v = [\eta]^{1.49} \cdot 5.37 \cdot 10^4$).

tion with hydrogen was close to 1, which agreed to the literature data for similar systems [16—19].

Table 3. Kinetic parameters of the chain transfer reaction with hydrogen

Titanium compound in catalyst	Ti content wt. %	$(k_{tr}^H/k_p) \cdot 10^3$	Reference
$[\eta^6\text{-benzeneTiAl}_2\text{Cl}_8]$ (cat. I) ¹⁾	0.7	10.0	this work
TiCl_4 (cat. III) ¹⁾	1.1	9.1	[19]
TiCl_4 (cat. III) ¹⁾	2.0	13.3	this work
$\text{Ti}(\text{OEt})_2\text{Cl}_2$ (cat. IV) ²⁾	2.0	8.4	this work

¹⁾ TIBA as cocatalyst. ²⁾ TEA as cocatalyst.

The oxidation state of titanium in the active component of catalyst and modification of titanium compound by OR groups have no significant effects on the k_{tr}^H/k_p ratio (Table 3). As compared to catalysts I and III, a distinctive feature of catalyst IV containing titanium diethoxydichloride as the active component is that it produces PE with a narrowed MWD ($M_w/M_n = 4.5$) at a high concentration of H_2 ($\text{H}_2/\text{C}_2\text{H}_4$ ratio = 1) (Table 2). Under these conditions, catalysts I and III with titanium (II) and (IV) chlorides produced PE with a broadened MWD ($M_w/M_n = 6.7\text{—}8.0$).

Ethylene copolymerization with 1-hexene in the presence of TMC catalysts having different active components

For each of TMC under consideration, the introduction of 1-hexene into polymerization medium ($[\text{C}_6\text{H}_{12}] = 0.16\text{—}0.64$ M) gave a 2 to 3 times increase in activity as compared to ethylene homopolymerization. The data concerning the effect of 1-hexene concentration on the composition of copolymers obtained were used to calculate copolymerization ratio of ethylene $r_1 = k_{11}/k_{12}$ (k_{11} is the rate constant of ethylene addition to ethylene unit of the propagating chain, k_{12} is the rate constant of 1-hexene addition to ethylene unit of the propagating chain) according to the method suggested elsewhere [20, 21].

Table 4 presents the values of r_1 for supported catalysts I, II, III and IV. One may see that r_1 values are virtually similar for catalysts II, III and IV, containing Ti^{3+} or

Ti^{4+} as the active components. Catalyst I, comprising Ti^{2+} compound, shows a lower r_1 value, which corresponds to a higher copolymerization ability in the presence of this catalyst.

Table 4. Values of the ethylene copolymerization ratio (r_1) for ethylene/1-hexene copolymerization in the presence of catalysts of different compositions^{a)}

Titanium compound in catalyst	r_1	Reference
$[\eta^6\text{-benzeneTiAl}_2\text{Cl}_8]$ (cat. I)	65	this work
$\text{TiCl}_3 \cdot n\text{DBE}$ (cat. II)	110	this work
TiCl_4 (cat. III)	100	[20]
$\text{Ti}(\text{OEt})_2\text{Cl}_2$ (cat. IV)	114	this work

^{a)} Polymerization conditions: heptane, TIBA as cocatalyst, temp. 80 °C, ethylene pressure 0.4 MPa (4 bar), hydrogen pressure 0.1 MPa (1 bar), $[\text{C}_6\text{H}_{12}] = 0\text{—}0.64$ M, time 15—60 min.

CONCLUSIONS

— Highly active supported catalytic systems for ethylene polymerization can be produced using Ti(II), Ti(III) and Ti(IV) compounds as catalysts. Among them, the catalytic systems comprising Ti(II) complex $[\eta^6\text{-benzeneTiAl}_2\text{Cl}_8]$ shows a maximum activity. The active sites (AS) are formed as a result of the interaction of AOC with such Ti-compounds.

— Oxidation state of the initial titanium compound used for preparation of AS has only a slight effect on the molecular weight (controlled by hydrogen) and MWD of PE produced. Presumably, a broad MWD of PE synthesized in the presence of these catalysts relates not to a differing oxidation states of titanium in AS, but rather to heterogeneity of AS caused by the formation of different coordination (structural) states of titanium in AS due to interaction of the active component with the support — magnesium chloride.

— Changes in the ligand environment of titanium compound (introduction of OR groups) have a pronounced effect on M_w and MWD of PE and lead, in particular, to a narrow MWD .

— Titanium-magnesium catalyst produced with Ti(II) compounds of $[\eta^6\text{-benzeneTiAl}_2\text{Cl}_8]$ composition shows the enhanced copolymerization ability in ethylene copolymerization with 1-hexene.

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