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Titanium-magnesium catalysts containing tetrahydrofuran and ethyl acetate for ethylene polymerization

Summary — A complex $[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]$ (I) was used as a precursor of titanium-magnesium catalysts for ethylene polymerization. The complex was ball-milled in hexane with $[\text{MgCl}_2(\text{THF})_2]$ and activated with AlEt_3 used as cocatalyst for 15 min at 323 K. Ethylene was polymerized at 323 K in hexane at a pressure of 0.5 MPa. The reaction was quenched with methanolic 5% HCl and the polymer was washed with methanol and dried at 303 K for 12 h at 5 hPa. The catalyst was found to be very active. Depending on the nature of the cocatalyst used, the catalyst activity varied within a range of 21.5–93.0 kg PE/(g Ti · h) and the resulting polymer was characterized by specific gravity 0.955–0.968 g/cm³, bulk density 115–128 g/dm³, crystallinity 57.5–61.7% and molecular weight distribution width 9.04–11. The complex (I) is believed to decompose at the catalyst preparation step. Catalyst activities of (I) were compared with those of catalysts based on titanium(III) and titanium(IV) chlorides and their complexes with Lewis bases. Pure (I) activated with organoaluminum compound is inactive in low-pressure ethylene polymerization.

Key words: $[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]$ as precursor of Ti-Mg catalysts, ethylene polymerization, catalyst activity, polymer properties.

Titanium-magnesium catalysts containing organic Lewis bases (ethers, esters, *etc.*) show high catalytic activities in low-pressure ethylene polymerization [1–3]. They have greatly altered the production of polyolefins. The literature on Ziegler–Natta catalysis abounds with data on modification of the catalysts. There are several modifications, *viz.*, increase in catalyst activity, improvement of the stereoregulating ability, enhancement of stability, change of polymer particle size, *etc.* The role of the Lewis base in these catalysts is still not clear. The Lewis base (a typical electron donor) has been suggested to control the stoichiometry of the catalyst, to stabilize active centers, to have a stereoregulating capability, *etc.* [4, 5]. Some efforts have been undertaken to explain the role of magnesium dichloride [6] and tetrahydrofuran [7] in the catalysts.

Addition of a Lewis base to the catalytic system results in a substantial increase in the catalytic activity and in improvement of polyolefin steric composition. Magnesium dichloride, usually used as a support, forms complexes with different Lewis bases, *e.g.* tetrahydrofuran, ethyl acetate, ethyl benzoate, and ethanol

[8, 9]. Ethyl acetate is a promising Lewis base, from the catalytic point of view, because it reacts not only with MgCl_2 and TiCl_4 but also with organoaluminum compounds. Moreover, it forms a bimetallic titanium-magnesium complex $[(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)_4\text{Mg}(\mu\text{-Cl})_2\text{TiCl}_4]$ [10]. Such complexes are most likely to form during the preparation of titanium-magnesium catalysts containing ethyl acetate.

This paper sets out to describe studies on ethylene polymerization over a titanium-magnesium catalyst prepared from the complex $[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]$ as a precursor.

EXPERIMENTAL

Preparation of, and manipulations with, the catalysts were always carried out under dry, oxygen-free argon by using the standard inert atmosphere technique [11].

Materials

Ethylene (Blachownia, Kędzierzyn-Koźle) was purified in columns packed with sodium supported on Al_2O_3 and over 4 Å molecular sieves.

Pure-grade argon (99.995%) (Liquid Carbonic, Po-

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land) was used after having been passed through a column of sodium supported on Al_2O_3 .

Pure-grade hexane (Petrochemia Plock SA, Plock) was refined with sulfuric acid, dried with KOH, and refluxed from sodium metal and benzophenone in an argon atmosphere and stored over 4 Å molecular sieves.

Triethylaluminum, diethylaluminum chloride, sesquiethylaluminum chloride and triisobutylaluminum (Fluka's pure grade) were used without further purification.

Titanium trichloride, hydrogen-reduced form (Aldrich).

Titanium tetrachloride (Aldrich).

Complex $[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]$ (I) was prepared by Sobota *et al.* [12].

Complexes $[\text{TiCl}_3(\text{THF})_3]$ (II), $[\text{TiCl}_4(\text{THF})_2]$ (III) and $[\text{TiCl}_4(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)_2]$ (IV) were prepared according to [13].

Catalyst preparation

Titanium chloride complex (I–IV) was ball-milled in a slurry with a magnesium dichloride complex $[\text{MgCl}_2(\text{THF})_2]$ and activated with an organoaluminum compound. For example, 10 mmols of $[\text{MgCl}_2(\text{THF})_2]$ was ball-milled in a slurry (hexane, 100 ml) with 1 mmol of titanium chloride complex for 24 h. The sample of the precatalyst (0.01 mmol Ti) was activated with 20 mmol of AlEt_3 for 15 min at 323 K.

Polymerization of ethylene

Ethylene polymerization was carried out at 323 K in a stainless steel reactor (1 dm³) equipped with a stirrer, in hexane at a pressure of 0.5 MPa. The polymerization reaction was quenched with a 5% solution of HCl in methanol (150 ml). The polymer was filtered off, washed with methanol and dried at 303 K for 12 h at reduced pressure (5 hPa).

Methods of polyethylene characterization

Molecular weight and molecular weight distribution of polyethylene were determined by GPC (Waters Model 150-C).

Specific density of polyethylene was determined ac-

ording to the Polish Standard PN-80/C-89035 at 296 K.

Bulk density of polyethylene was determined according to the Polish Standard PN-80/C-04532.

Crystallinity (by IR) of polyethylene was estimated according to the absorbance bands of ω_{CH_2} in the crystalline ($\nu = 730 \text{ cm}^{-1}$) and amorphous ($\nu = 718 \text{ cm}^{-1}$) phases of PE which were recorded with a FTIR U9800 Philips Spectrometer.

Crystallinity and melting temperature of polyethylene were estimated with a 2010 TA Instruments DSC calorimeter.

RESULTS AND DISCUSSION

The catalyst studied shows varying activities depending on the nature of the cocatalyst used (Table 1). The highest activity was achieved when an equimolar mixture of AlEt_2Cl and AlEt_3 was used for the activation of the catalyst. Cocatalyst's type was shown to affect the properties of polyethylene as follows: specific density varied within the range 0.955 to $0.968 \text{ g} \cdot \text{cm}^{-3}$, crystallinity (by IR) 47–56.6% and 57.5–61.7% (by DSC), bulk density 115 – $128 \text{ g} \cdot \text{dm}^{-3}$, molecular weight distribution 9–11. The catalyst was active from the very beginning of the reaction and, past a soft maxi-

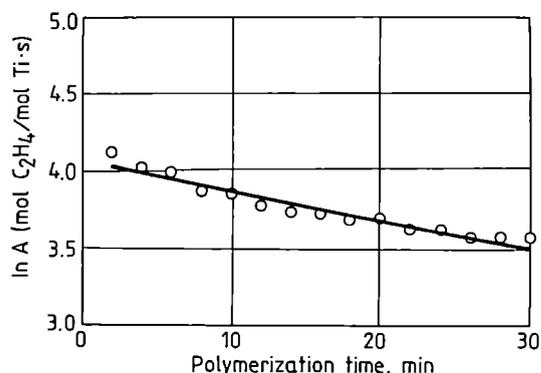


Fig. 1. Catalyst activity in ethylene polymerization vs. time; catalytic system: $[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]/\text{AlEt}_2\text{Cl}/\text{AlEt}_3$; $[\text{Ti}] = 0.01 \text{ mmol} \cdot \text{dm}^{-3}$; $[\text{Al}] = 10 \text{ mmol} \cdot \text{dm}^{-3}$; $\text{AlEt}_2\text{Cl}:\text{AlEt}_3 = 1:1$; $\text{Mg}:\text{Ti}$ mole ratio = 10:1; $P = 0.5 \text{ MPa}$

Table 1. The results of ethylene polymerization in the presence of the catalytic system: $[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{AcOEt})]/\text{cocatalyst}$; $[\text{Ti}] = 0.01 \text{ mmol} \cdot \text{dm}^{-3}$; $[\text{Al}] = 20 \text{ mmol} \cdot \text{dm}^{-3}$; $\text{Mg}:\text{Ti}$ mole ratio = 10:1; $P = 0.5 \text{ MPa}$

Catalytic system	Activity $\text{kg PE (g Ti} \cdot \text{h)}^{-1}$	Polyethylene				
		density ^{a)} $\text{g} \cdot \text{cm}^{-3}$	C ^{b)} %	C ^{c)} %	bulk density ^{d)} $\text{g} \cdot \text{dm}^{-3}$	MWD ^{e)}
$[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{AcOEt})]/\text{AlEt}_3$	67.0	0.965	47.0	61.7	128	9.04
$[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{AcOEt})]/\text{AlEt}_2\text{Cl}$	21.5	0.955	46.9	60.1	115	9.48
$[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{AcOEt})]/\text{AlEt}_2\text{Cl}/\text{AlEt}_3$ ^{*)}	93.9	0.968	56.6	57.5	119	1.46
$[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{AcOEt})]/\text{Al}(i\text{-Bu})_3$	87.3	0.964	47.2	60.5	117	10.99

^{a)} Polish Standard PN-80/C-89035. ^{b)} Crystallinity by FTIR PU 9800 Philips. ^{c)} Crystallinity by DSC 2010 TA Instruments. ^{d)} Polish Standard PN-80/C-04532, ^{e)} WATERS 150-C. ^{*)} $\text{AlEt}_2\text{Cl}:\text{AlEt}_3$ mole ratio = 1:1.

imum, its activity lowered on account of deactivation processes (Fig. 1). The deactivation was found to be a first-order reaction with a rate constant $2.57 \cdot 10^{-4} \cdot \text{s}^{-1}$ (correlation factor = 0.937).

Experimental data show organoaluminum compounds to participate in the reaction of polymer chain transfer (Fig. 2). The molecular weight distribution of poly-

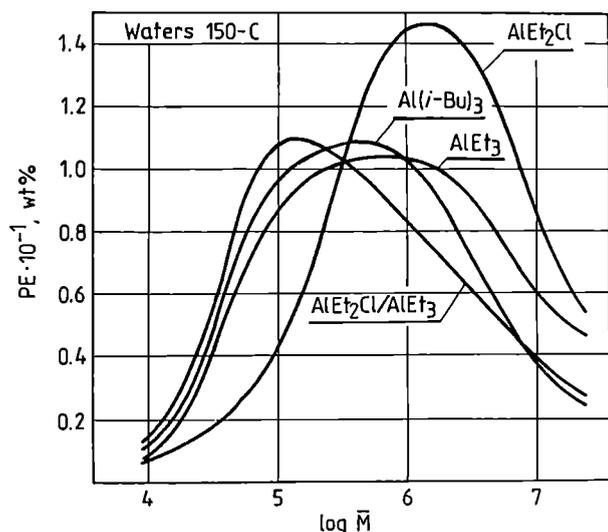


Fig. 2. The effect of cocatalyst nature on molecular weight distribution of PE, catalyst: $[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]/\text{cocatalyst}$; $[\text{Ti}] = 0.01 \text{ mmol} \cdot \text{dm}^{-3}$; $[\text{Al}] = 10 \text{ mmol} \cdot \text{dm}^{-3}$; $\text{Mg}:\text{Ti}$ mole ratio = 10:1; $P = 0.5 \text{ MPa}$

ethylene (MWD) varies with the concentration of the organoaluminum compound. The MWD of polyethylene is wide and the range of molecular weight changes with the nature of the cocatalyst (Fig. 2). With AlEt_2Cl substituted for AlEt_3 as cocatalyst, the molecular weight shifted towards higher values. MWD shape variations seem to be caused by changes in the chain transfer reaction. Trialkylaluminum is known to be a much better chain transfer agent than chloride-containing organoaluminum compounds [14]:

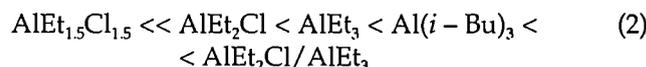


where: Ti — denotes a catalytic center; $-\text{CH}_2\text{CH}_2\text{R}$ — polymer chain.

There are two basic explanations for wide MWD of polyolefins [14]: one is the physical phenomena affecting the polymerization process and increasing the MWD; and the other is the chemical reactions. The physical factors include diffusion and polymer-solvent interactions in the polymerization reaction. The active centers, containing the growing polymer chains in the solution, give rise to a widened MWD. Chemical factors are those of growing polymer chain transfer.

The catalytic activity of the system varies over a wide

range (Table 1) depending on the nature of the organoaluminum cocatalyst:



The best single cocatalyst was triisobutylaluminum, whereas sesquiethylaluminum chloride was completely inactive. Such activity alterations can be attributed to the following: the ethylene polymerization rate constants assume different values affected by the nature of the organoaluminum compound; the concentrations of active centers and the alkylating and reducing powers of the cocatalyst are different. The mixtures of organoaluminum compounds used initially were AlEt_2Cl and AlEt_3 or AlEt_2Cl and $\text{Al}(i-\text{Bu})_3$ (Fig. 3). Catalyst activity

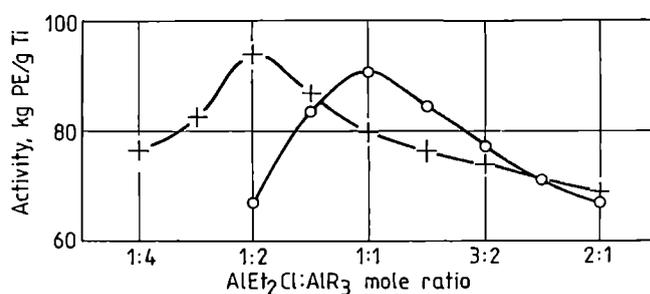


Fig. 3. The effect of AlEt_2Cl to AlR_3 mole ratio on ethylene polymerization in the presence of the catalytic system: $[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]/\text{cocatalyst}$; cocatalyst: o — $\text{AlEt}_2\text{Cl}/\text{AlEt}_3$, + — $\text{AlEt}_2\text{Cl}/\text{Al}(i-\text{Bu})_3$, $[\text{Ti}] = 0.01 \text{ mmol} \cdot \text{dm}^{-3}$; $[\text{Al}] = 10 \text{ mmol} \cdot \text{dm}^{-3}$; $\text{Mg}:\text{Ti}$ mole ratio = 10:1; $P = 0.5 \text{ MPa}$

rose after certain $\text{AlEt}_2\text{Cl}:\text{AlR}_3$ mole ratio has been achieved and then progressively decreased to the level typical for the system activated by AlEt_3 or $\text{Al}(i-\text{Bu})_3$. The highest activity was achieved for the equimolar (1:1) mixture of AlEt_2Cl and AlEt_3 added in this order to the catalyst. For the mixture of AlEt_2Cl and $\text{Al}(i-\text{Bu})_3$, the optimum mole ratio is 1:2. Variation of the molecular weight (MW) of polyethylene as the $\text{AlEt}_2\text{Cl}:\text{AlEt}_3$ mole ratio is increased, associated with the variation of the polymer chain transfer reaction, is also presented in Fig. 3. Mole *et al.* [15] have found that the $\text{AlEt}_2\text{Cl}:\text{AlEt}_3$ mixture exists in the equilibrium:



The existence of the equilibrium (3), affecting the nature of the organoaluminum compounds, does not explain the experimental data observed. Presumably, the equilibrium is more complex. One explanation can be the variation of heterogeneous catalyst activity with the type of organometallic compound. The data (Fig. 3) allow to see that the organometallic compounds do participate in the structure of active centers. In many cases, this participation in the active center structure is reversible and can be described as an equilibrium adsorption

with a very high adsorption constant. Organoaluminum compounds are believed to become adsorbed on active centres in the form of associates, usually dimers rather than monomeric unit forms.

In many cases organoaluminum compounds not only form active centers but also can decrease their number (Fig. 4). These phenomena are especially pronounced in

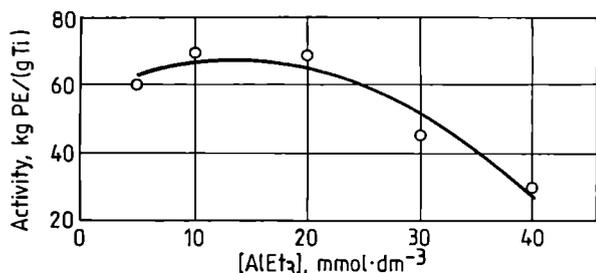


Fig. 4. The effect of triethylaluminum concentration on ethylene polymerization, catalytic system: $[MgCl_2(THF)_2]/[TiCl_3(THF)_2(CH_3CO_2C_2H_5)]/AlEt_3$; $[Ti] = 0.01 \text{ mmol} \cdot \text{dm}^{-3}$; $Mg:Ti$ mole ratio = 10:1; $P = 0.5 \text{ MPa}$

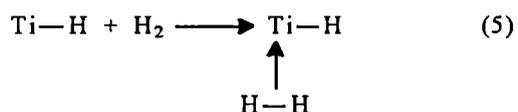
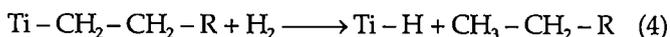
highly active supported catalysts and they are partially responsible for the instability of these catalysts. Two different effects can be distinguished: an irreversible destruction of active centres (mainly due to the further reduction of a transition metal) and the reversible poisoning of active centers by products of organometallic compound transformation.

Hydrogen is a very effective agent controlling polymer chain growth (4). However, it lowers the catalytic activity (Table 2). Partial deactivation (inhibition) of ac-

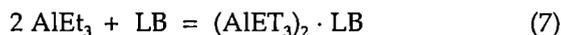
Table 2. The effect of hydrogen on ethylene polymerization and molecular weight of polyethylene; catalyst $[MgCl_2(THF)_2]/[TiCl_3(THF)_2(AcOEt)]/AlEt_2Cl/AlEt_3$; $[Ti] = 0.05 \text{ mmol} \cdot \text{dm}^{-3}$; $Al:Ti$ mole ratio = 500:1; $AlEt_2Cl:AlEt_3$ mole ratio = 1:1; polymerization time = 15 min

P_{H_2} , MPa	Activity kg PE $\cdot (\text{g Ti} \cdot \text{h})^{-1}$	M_n	M_w	M_w	M_z
0.00	83.52	121 462	366 732	425 048	1 589 332
0.05	75.16	96 807	329 611	382 956	1 396 015
0.10	65.14	77 816	309 389	375 522	901 972
0.15	58.46	55 965	238 708	289 219	860 277
0.20	48.33	43 314	199 019	232 768	567 584

tive centers can be caused by further adsorption of hydrogen to the titanium hydride (5):



The role of ethyl acetate (Lewis base, LB) in the titanium-magnesium catalytic system studied is not clear. Ethyl acetate is known to form complexes with magnesium dichloride [8] and titanium chlorides [13]. We have found FTIR spectroscopy (Yoe-Jones method) that $AlEt_3$ or $AlEt_2Cl$ and ethyl acetate form complexes. Guyot [16] has proposed at least two equilibria to form between trialkylaluminum and organic ester:



The stoichiometry of $AlEt_3:CH_3CO_2C_2H_5$ interaction [14] was found to be 2:1, whereas for the mixture $AlEt_2Cl:CH_3CO_2C_2H_5$ it was 1:1.

There is a slight increase in the catalytic activity as the amount of ethyl acetate as an internal Lewis base is increased in the catalytic system obtained from pure titanium(III) chloride (Fig. 5). Within the range of $CH_3CO_2C_2H_5:Ti$ mole ratios from 1:10 to 2:1, the catalytic activity changes within 15 kg PE $(\text{g Ti} \cdot \text{h})^{-1}$.

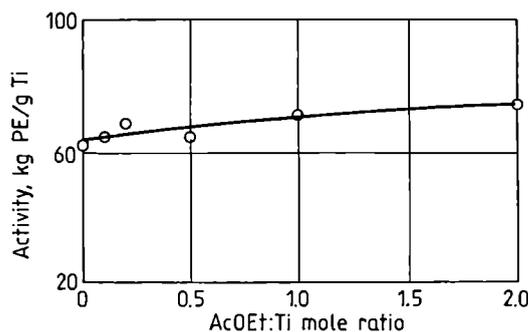


Fig. 5. The effect of ethyl acetate as an internal Lewis base on the activity of the catalytic system $[MgCl_2(THF)_2]/[TiCl_3]/CH_3CO_2C_2H_5/AlEt_3$ in ethylene polymerization; $[Ti] = 0.01 \text{ mmol} \cdot \text{dm}^{-3}$; $[Al] = 10 \text{ mmol} \cdot \text{dm}^{-3}$; $Mg:Ti$ mole ratio = 10:1; $P = 0.5 \text{ MPa}$

There is no significant difference in the catalytic activities of the catalytic systems based on complex (I) and those obtained from titanium(III) or titanium(IV) chlorides (Table 3). On the other hand, the catalysts prepared from complexes $[TiCl_3(THF)_3]$ (II), $[TiCl_4(THF)_2]$ (III) or $[TiCl_4(CH_3CO_2C_2H_5)_2]$ (IV) show much lower activities. Presumably, the lower donor number $D_{II} = 16.5$ for ethyl acetate compared with that THF ($D_{II} = 20$) [17], results in the greater portion of the complex $[TiCl_3(THF)_2(CH_3CO_2C_2H_5)]$ partially decomposed during the catalyst preparation step to yield an unsaturated complex $[TiCl_3(THF)_2]$, thus giving the more active catalyst than that obtained from $[TiCl_3(THF)_3]$. Except for density, there is no substantial effect of the precursor type on the other properties of the polyethylene obtained.

All heterogeneous Ziegler-Natta catalysts are very

Table 3. The effect of type of titanium precursor on ethylene polymerization. Catalytic system: $[\text{MgCl}_2(\text{THF})_2]/\text{precursor}/\text{AlEt}_3$; Mg:Ti mole ratio = 10:1; $P = 0.5 \text{ MPa}$; $[\text{Ti}] = 0.01 \text{ mmol} \cdot \text{dm}^{-3}$; $[\text{Al}] = 20 \text{ mmol} \cdot \text{dm}^{-3}$

Precursor	Activity, kg PE $\cdot (\text{g Ti} \cdot \text{h})^{-1}$	Polyethylene				
		density ^{a)} $\text{g} \cdot \text{cm}^{-3}$	$C^{b)}$, %	$C^{c)}$, %	bulk density ^{d)} $\text{g} \cdot \text{dm}^{-3}$	MWD ^{e)}
$[\text{TiCl}_3(\text{THF})_2(\text{AcOEt})]$ (I)	67.00	0.965	47.0	61.7	128	9.04
$[\text{TiCl}_3(\text{THF})_3]$ (II)	28.62	0.952	47.0	59.1	111	6.40
$[\text{TiCl}_4(\text{THF})_2]$ (III)	24.30	0.958	46.4	57.0	125	8.62
$[\text{TiCl}_4(\text{AcOEt})_2]$ (IV)	36.80	0.961	47.8	61.3	116	8.15
TiCl_3	64.30	0.948	49.3	60.1	120	7.43
TiCl_4	69.60	0.946	46.9	53.5	117	7.15

a), b), c), d), e) — see Table 1 for explanations.

sensitive to the majority of organic and inorganic substances. Most chemical substances reduce the catalytic activity drastically or deactivate the catalyst completely. They can be regarded as classical catalytic poisons. Studies on poisoning of Ziegler—Natta catalysts help us understand some important features of the catalytic polymerization of olefins, mainly the quantitative estimation of active center concentration in these catalysts. Carbon disulfide is a very effective poison for heterogeneous Ziegler—Natta catalysts [18, 19]. Infrared studies have shown that no chemical reaction takes place between CS_2 and organoaluminum compounds [20]. The active center concentration in the $[\text{MgCl}_2(\text{THF})_2]/[\text{TiCl}_3(\text{THF})_2(\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5)]/\text{AlEt}_2\text{Cl}/\text{AlEt}_3$ catalytic system estimated *via* inhibition of ethylene polymerization with carbon disulfide, was found to be *ca.* 25% of the initial concentration of titanium in the polymerization medium [14]. The well-known equation of polymerization rate $R_p = k_p [C][M]$ ($[C]$ = active center concentration, $[M]$ = monomer concentration) allowed to evaluate the rate constant k_p as $394 \text{ dm}^3 \cdot (\text{mol} \cdot \text{s})^{-1}$ for the polymerization reaction.

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