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State of Titanium in Supported Titanium–Magnesium Catalysts for Propylene Polymerization

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Abstract—The oxidation state of titanium and the coordination state of Ti^{3+} ions in $TiCl_4/D_1/MgCl_2$ (D_1 is a phthalate) supported titanium–magnesium catalysts (TMCs) after the interaction with an $AlEt_3/D_2$ cocatalyst (D_2 is propyltrimethoxysilane or dicyclopentyldimethoxysilane) were studied by chemical analysis and EPR spectroscopy. Different oxidation state distributions of titanium ions were observed in the activated catalyst and mother liquor: Ti^{3+} and Ti^{2+} ions were predominant in the activated catalyst and mother liquor, respectively. The effects of interaction conditions (reaction temperature and time and Al/Ti and D_2/Ti molar ratios) of TMCs with the cocatalyst on the state of titanium in activated samples were studied. The interaction of TMCs with the cocatalyst decreased the titanium content and caused the appearance of aluminum in the activated sample, which was most clearly pronounced at a temperature of 25°C and occurred within the first 10 min of treatment. An increase in the temperature to 70°C and an increase in the interaction time to 60 min only slightly affected the concentrations of titanium and aluminum. The presence of D_2 as a cocatalyst constituent facilitated the removal of titanium compounds and restricted the adsorption of aluminum compounds on the catalyst surface. The main fraction of titanium consisted of Ti^{3+} ions (62–89%), and the rest was Ti^{4+} ions (22–35%) under mild interaction conditions (25°C; Si/Ti = 25) or Ti^{4+} (0–21%) and Ti^{2+} (9–21%) ions under more severe conditions (50 or 70°C; Si/Ti from 0 to 5). According to EPR-spectroscopic data, at D_2/Ti from 1 to 5, Ti^{3+} ions mainly occurred as associates, whereas they occurred as isolated ions at D_2/Ti = 25. The initial and activated catalysts were similar in activity in the reaction of propylene polymerization, and titanium compounds, which were removed from the catalyst upon interaction with $AlEt_3/D_2$, were inactive in this process.

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INTRODUCTION

Highly efficient supported titanium–magnesium catalysts (TMCs) are currently used in polypropylene (PP) production. They contain titanium tetrachloride as an active component on a support of highly dispersed magnesium dichloride. A stereoregulating electron-donor compound (internal donor D_1) is also a constituent of the catalyst. To activate the catalysts, they are brought into interaction with a cocatalyst—an organoaluminum compound (OAC) in combination with an additional stereoregulating electron-donor compound (external donor D_2). In general, the catalytic system has the following composition: $TiCl_4/D_1/MgCl_2–AlEt_3/D_2$. It is well known that, upon the interaction of TMCs with the cocatalyst, new titanium–alkyl bonds appear and titanium tetrachloride is reduced to form titanium compounds in different oxidation states (Ti^{4+}, Ti^{3+}, and Ti^{2+}). To quantitatively determine the concentrations of titanium ions in different oxidation states in TMCs, both well-known chemical methods, in particular, chelatometric and redox titration [1–7], and physical techniques, such as EPR [2, 8–11] and X-ray photoelectron spectroscopy (XPS) [12–14], are used. The advantages of chemical analysis are the accurate determination of the volume of a titrant reagent with a known concentration consumed for the interaction with the test ions Ti^{n+} (n = 2 or 3), the high rate of reaction, and the well-defined detection of the instant of reaction completion (by an indicator color change). However, this method is applicable only on condition that the oxidation state of titanium remains unchanged upon dissolving the catalyst and the solutions are transparent and colorless. EPR spectroscopy provides information on the amount and coordination state of Ti^{3+} ions; that is, it allows one to determine whether these are isolated Ti^{3+} ions or Ti^{3+} ions in an associated state. Zakharov et al. [8] found that the total amount of Ti^{3+} ions in TMCs after contact with an OAC can be determined by EPR spectroscopy after an additional treatment of the catalyst with pyridine (this procedure was also used more recently [9, 10]). The concentration of Ti^{2+} ions is found by converting them into Ti^{3+} ions using the consecutive treatment of the activated catalyst with pyridine, then with water or pentafluorochlorobenzene, and next with pyridine. The use of XPS for identifying the oxidation state of titanium in TMCs is based on the determination of the binding energy of electrons and the Ti $2p_{3/2}$ peak width at half height at a maximum intensity.

Quantitative data on the oxidation state of titanium in TMCs from numerous publications [1–10, 12–15] are difficult to compare with each other because they were obtained not only using different methods but also at different support and catalyst compositions and preparation procedures. However, we can make the following general conclusions:

(1) The oxidation state of titanium depends on the composition of a catalyst, the presence of an internal donor in the catalyst, and the conditions of the interaction of the TMC with the cocatalyst.

(2) Upon the interaction of the TMC with the cocatalyst, the Ti^{4+} ions are reduced with the formation of Ti^{3+} compounds. Under certain conditions, a portion of titanium remains as Ti^{4+} and the other portion is converted into Ti^{2+} species.

(3) Data obtained by EPR spectroscopy and chemical analysis indicate that the Ti^{3+} compounds formed upon the interaction with an OAC occur as catalyst constituents in various coordination states. The major portion of these compounds occurs as associates, which do not give signals in the EPR spectrum, whereas a smaller portion occurs as isolated Ti^{3+} ions.

(4) In a number of publications [8, 9, 11, 16], it was found that the interaction of TMCs with OAC results in the transfer of a portion of titanium chloride from a solid catalyst to the mother liquor.

Almost all of the quantitative data on the concentrations of titanium in various oxidation states in activated catalysts were obtained by analyzing a reaction mixture (an activated solid catalyst in combination with a liquid phase) without considering the fact that a portion of titanium passed into a liquid phase under conditions of the interaction of the initial sample with the cocatalyst; consequently, the titanium content of the activated catalyst decreased. At the same time, these data were attributed to the activated catalyst [1–8, 10, 11, 15].

In this study, we used two samples of modern, highly efficient TMCs containing dibutyl phthalate and diisobutyl phthalate and activated with $AlEt_3$ or $AlEt_3$ in combination with an external donor (D_2) as an example. We obtained data on the oxidation state of titanium in the activated catalyst using a two-step redox titration procedure [4]. The catalysts belong to fourth-generation TMCs. They exhibit high activity (to provide a yield of >20 kg PP/(g catalyst) or 1000 kg PP/(g Ti)) and high stereospecificity, and they are characterized by a controlled morphology of catalyst particles. These particles have a required size; they are characterized by a narrow particle-size distribution and possess a high density. We were the first to study the oxidation-state distribution of titanium ions both in the total reaction mixture (the solid catalyst with the liquid phase) and in the activated solid catalyst. We also studied the effect of the interaction conditions (temperature, interaction time, and Al/Ti and D_2/Ti molar ratios) of TMCs with a cocatalyst on the distribution of titanium in various oxidation states in the activated solid catalyst taking into account the circumstance that a portion of titanium passed from the solid catalyst into solution upon the interaction with the OAC.

EXPERIMENTAL

Catalysts

The $TiCl_4/D_1/MgCl_2$ TMCs, where D_1 is an internal donor, namely, dibutyl phthalate (DBP) or diisobutyl phthalate (DIBP), were used in this study. The catalysts differed in preparation conditions and titanium contents. Catalyst **1** ($TiCl_4$/DBP/$MgCl_2$, 2.0 wt % Ti and 12 wt % DBP) was prepared in accordance with a published procedure [17], whereas catalyst **2** ($TiCl_4$/DIBP/$MgCl_2$, 2.4 wt % Ti and 10.5 wt % DIBP) was prepared in accordance with a published procedure [18].

The reagents used in the synthesis of the catalysts and in the treatment of them with a cocatalyst were preliminarily purified to remove moisture and oxygen to polymerization purity using well-known methods. They were kept and used in an atmosphere of an inert gas (argon).

Catalyst Treatment with a Cocatalyst (Activation Step)

Heptane, an appropriate amount of $AlEt_3$, and, if necessary, an external donor D_2, namely, propyltrimethoxysilane (PTMS) or dicyclopentyldimethoxysilane (DCPDMS), were introduced into a 1 l glass reactor, which was placed in a thermostated bath, at room temperature in a flow of argon. The contents of the reactor were heated to a specified temperature with stirring; thereafter, a known amount of a catalyst was added. The reaction mixture was kept at the specified temperature for a certain time and then rapidly cooled to 20°C. Next, the liquid phase (mother liquor) was decanted and the catalyst residue was repeatedly washed with heptane and dried in a vacuum. Finally, the total concentrations of titanium and aluminum and the concentrations of titanium in different oxidation states were determined in the dry catalyst.

Catalysts **1** and **2** were treated with the cocatalyst ($AlEt_3$ or $AlEt_3/D_2$) at temperatures from 25 to 70°C; Al/Ti and D_2/Ti molar ratios from 10 to 100 and from 0 to 25, respectively; and reaction time of 10, 30, or 60 min.

Chemical Analysis

The total concentrations of titanium and aluminum were measured by inductively coupled plasma atomic emission spectrometry (ICP AES) on an Optima 4300 DV spectrometer.

The concentrations of titanium in different valence states were determined using a published procedure [4], which involved two-step redox titration in accordance with procedures **A** or **B**. As applied to the analysis of our samples, this procedure was somewhat changed: (1) in the titration according to procedure **A**, concentrated sulfuric acid was used in place of toluene to prepare a 1% solution of *N*,*N*'-diphenylbenzidine as an indicator; (2) in the course of both of the procedures, the sequence and amounts of introduced reagents were changed.

The titration was performed in a 250-ml glass reactor equipped with a magnetic stirrer in an atmosphere of argon. All of the solvents and reagent solutions were purged with pure argon before each particular titration.

Procedure A. A known catalyst amount (0.2–0.4 g) was added to a mixture containing 40 ml of H_2O and 10 ml of a 0.1 N solution of $NH_4Fe(SO_4)_2$ with stirring. The temperature of the mixture was increased to 50°C and maintained until the complete dissolution of the catalyst. After holding the resulting solution for 10–15 min, 40 ml of concentrated H_3PO_4 (85%) was added to it; as a result of this, Ti^{2+} and Ti^{3+} ions were oxidized to Ti^{4+} by Fe^{3+} ions. In turn, the Fe^{3+} ions were reduced to Fe^{2+} according to the reactions

$$Ti^{2+} + 2Fe^{3+} \longrightarrow Ti^{4+} + 2Fe^{2+};$$

$$Ti^{3+} + Fe^{3+} \longrightarrow Ti^{4+} + Fe^{2+}.$$

Then, 0.05 ml of an indicator (1% solution of *N*,*N*'-diphenylbenzidine in concentrated sulfuric acid) was added to the solution and Fe^{2+} ions were titrated with a 0.1 N solution of $K_2Cr_2O_7$:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O.$$

The titration end point was determined visually by a sharp solution color change from colorless to violet.

Total cations $[2Ti^{2+} + Ti^{3+}]$ were determined using procedure **A**.

Procedure B. A known catalyst amount (0.2–0.4 g) was added to a mixture containing 60 ml of oxygen-free H_2O and 6 ml of concentrated sulfuric acid with stirring. The mixture was heated to 50°C, kept for 10–15 min after the dissolution of the catalyst, and cooled to room temperature. Next, 1 ml of an indicator (1 g of sodium diphenylaminosulfonate in 50 ml of H_2O) was introduced into the solution and titration was performed with a 0.1 N solution of $K_2Cr_2O_7$. The titration end point was determined by a solution color change from violet to green. In this case, Ti^{2+} ions were initially oxidized to Ti^{3+} by protons:

$$Ti^{2+} + H^+ \longrightarrow Ti^{3+} + \tfrac{1}{2} H_2;$$

then, all of the Ti^{3+} ions were oxidized to Ti^{4+} by $Cr_2O_7^{2-}$ ions:

$$6Ti^{3+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Ti^{4+} + 2Cr^{3+} + 7H_2O.$$

The concentration $[Ti^{2+} + Ti^{3+}]$ was calculated in accordance with procedure **B**.

The concentration $[Ti^{2+}]$ was calculated as difference between the concentrations found in accordance with procedures **A** and **B** (**A** – **B**); the concentration $[Ti^{3+}]$ was found as the doubled concentration found in accordance with procedure **B** minus the concentration found in accordance with procedure **A** (2**B** – **A**); $[Ti^{4+}] = [Ti] - ([Ti^{2+}] + [Ti^{3+}])$. The fractions of titanium ions in various oxidation states *n* were calculated in rel % as $[Ti^{n+}]/[Ti]$, where [Ti] is the total titanium content of the sample, wt %.

To analyze a reaction mixture (i.e., the suspension of an activated catalyst in mother liquor), a superstoichiometric amount (with reference to $AlEt_3$) of isopropanol was added to the cooled reaction mixture after completion of the step of activation. Then, the concentration of reduced titanium was determined using procedures **A** and **B**.

Procedures **A** and **B** were tested with model samples of $TiCl_2$ and $TiCl_3$; the experimental results were found close to calculated data:

Sample	Titanium concentration, wt %				
	calculated	results of analysis			
		Ti (ICP AES)	Ti^{2+} (**A**)	Ti^{3+} (**A**)	Ti^{3+} (**B**)
$TiCl_2$	40.3	40.5	38.5	–	–
$TiCl_3$	31.0	29.3	–	29.1	31.3

EPR-Spectroscopy

The EPR spectra were recorded on a Bruker ER-200D spectrometer at a temperature of –196°C. A dry catalyst sample was sealed in a glass ampoule. Some samples were additionally pretreated with pyridine to convert Ti^{3+} ions from an associated into an isolated state [8, 9]. The concentration of Ti^{3+} ions was determined with the use of $CuCl_2 \cdot 2H_2O$ as a standard substance.

Propylene Polymerization

The polymerization of propylene was performed in a 0.7-l autoclave in a heptane medium under the following conditions: temperature, 70°C; total pressure, 5 atm; reaction time, 2 h; $[AlEt_3] = 4$ mmol/l; molar ratios, Al/Ti = 300 and Al/PTMS = 10; and H_2 content of a gas phase, 2 vol %.

RESULTS AND DISCUSSION

Ti^{n+} Concentrations in the Catalyst and Mother Liquor

To determine the concentration of Ti^{n+} in an activated catalyst, we analyzed both the total reaction mixture and the individual activated catalyst repeatedly washed with heptane.

Table 1. Concentrations of Ti^{n+} ions in the catalyst and mother liquor after the interaction of the catalyst with $AlEt_3$

Initial sample	Analytical sample	[Ti], wt %	[Al], wt %	Al/Ti, mol	Fraction of Ti^{n+}, %		
					Ti^{4+}	Ti^{3+}	Ti^{2+}
$TiCl_4$/DBP/$MgCl_2$ (catalyst **1**)	Initial	2.0	–	–	100	–	–
	Catalyst + mother liquor	2.0	–	50	0	69	31
	Activated catalyst	1.36	1.7	2.3	0	89	11
	Mother liquor	–	–	–	0	27	73
$TiCl_4$/EB/$MgCl_2$ [5]	Initial	2.45	–	–	–	–	–
	Catalyst + mother liquor	2.45	–	50	15	40	45

Note: Conditions of the interaction of the catalyst with $AlEt_3$: temperature, 70°C; time, 30 min; [Ti] = 6 mmol/l; Al/Ti = 50.

Table 1 summarizes data on the concentrations of titanium in various oxidation states in the $TiCl_4$/DBP/$MgCl_2$ catalyst (catalyst **1**) before and after its treatment with $AlEt_2$ and in a liquid phase (mother liquor). For comparison, published data [5] are given, which were obtained upon the analysis of the $TiCl_4$/EB/$MgCl_2$ system (EB = ethyl benzoate) under analogous conditions using two-step redox titration. From Table 1, it follows that, first, after the interaction of catalyst **1** with $AlEt_3$, its composition changed (the titanium content decreased from 2.0 to 1.36 wt % and 1.7 wt % aluminum appeared as a catalyst constituent) and, second, the complete reduction of Ti^{4+} ions to Ti^{3+} and Ti^{2+} was observed. In this case, different distributions of Ti^{n+} ions in the catalyst and mother liquor were observed. In the activated catalyst, reduced titanium mainly occurred as Ti^{3+} ions, whereas Ti^{2+} ions were predominant in the mother liquor.

Thus, the distribution of titanium ions in various oxidation states in a reaction mixture is inconsistent with the distribution of these ions in an activated catalyst. Consequently, the distribution of Ti^{n+} ions in an activated sample, which was found by Fregonese et al. [5] after the treatment of the $TiCl_4$/EB/$MgCl_2$ catalyst with triethylaluminum (Table 1), cannot be a reliable characteristic of this sample because the entire reaction mixture was analyzed without considering the transfer of a portion of reduced titanium compounds into a liquid phase. This conclusion can also be made with respect to publications [1–8, 10, 15], in which quantitative data on the concentrations of titanium in various oxidation states were obtained by the analysis of the entire reaction mixture and referred to only an activated catalyst. Note that Kim and Somorjai [14] reported an inconsistency of quantitative data on the concentrations of titanium in various oxidation states obtained using various analytical techniques. In our opinion, the reason can be both differences in the compositions and preparation procedures of the initial catalysts and the choice of different test samples (reaction mixture or activated catalyst). Thus, a TMC treated with alkylaluminums and washed to remove mother liquor was analyzed by XPS [12, 13]. Published data [1–8, 10, 15] on the distribution of titanium ions were obtained upon the analysis of an entire reaction mixture; consequently, the Ti^{n+} ions that occurred in both the activated catalyst and the mother liquor were taken into account.

Effect of the Catalyst–Cocatalyst Interaction Conditions on the Oxidation State of Titanium

We studied the effect of interaction conditions (temperature, time, and Al/Ti and D_2/Ti molar ratios) of catalysts **1** and **2** with a cocatalyst ($AlEt_3$, $AlEt_3/D_2$) on the concentrations of titanium in various oxidation states in the activated sample.

Table 2 summarizes data on the effect of interaction temperature on the concentrations of reduced titanium species in the activated catalyst, as determined by titration and EPR spectroscopy.

The interaction of catalyst **1** with $AlEt_3$/PTMS was accompanied by a decrease in the titanium content. It was observed even at 25°C (experiment 1), and then it insignificantly decreased as the temperature was increased to 70°C (experiments 2 and 3). Aluminum was a constituent of the activated catalyst; the aluminum content and the Al/Ti molar ratio changed only slightly depending on interaction temperature (experiments 1–3). Sample **1** treated only with $AlEt_3$ at high catalyst and $AlEt_3$ concentrations contained more aluminum, and the Al/Ti ratio in it increased (experiment 4).

The interaction of catalyst **2** with the $AlEt_3$/DCPDS cocatalyst also resulted in a decrease in the titanium content and the appearance of aluminum in the activated catalyst (experiment 5). Analogous results were also obtained previously [9, 11, 16, 19] in studies on the interaction of TMC samples that differed in preparation procedures, titanium contents, and internal donors, with $AlEt_3$ or a mixture of $AlEt_3/D_2$. Thus, qualitatively, this effect manifested itself regardless of catalyst preparation procedure, whereas the quantitative concentrations of components in activated samples depended on particular conditions of interaction with the cocatalyst.

The reduction of a considerable fraction of Ti^{4+} ions to the state of Ti^{3+} (78%) occurred even at 25°C. As the temperature was increased from 25 to 70°C, the

Table 2. Effect of the interaction temperature of a TMC with a cocatalyst on the composition, oxidation state, and coordination state of titanium in the activated catalyst

Experiment no.	Temperature, °C	[Ti]*, wt %	[Al], wt %	Al/Ti, mol	Fraction of Ti^{n+} (based on the results of titration), %			Fraction of Ti^{3+} (based on EPR-spectroscopic data)**, %
					Ti^{4+}	Ti^{3+}	Ti^{2+}	
Activated catalyst **1**								
1	25	1.5	0.83	1.0	22	78	0	17 (41)
2	50	1.4	0.8	1.0	18	70	12	30 (65)
3	70	1.3	0.6	0.84	17	62	21	17 (40)
4***	70	1.36	1.7	2.3	0	89	11	–
Activated catalyst **2**								
5	50	1.46	1.33	1.62	21	70	9	–
6	70	1.5	–	–	11	89		–

Note: Interaction conditions: [Ti] = 0.5–1.0 mmol/l; $[AlEt_3]$ = 7.5–10 mmol/l; molar ratio Si/Ti = 1–5; and duration, 30 min.
* The total titanium content of the activated catalyst.
** The fraction of Ti^{3+} ions in the activated catalyst additionally treated with pyridine is given in parentheses.
*** The catalyst was treated with only $AlEt_3$ (with no external donor) at [Ti] = 6 mmol/l and $[AlEt_3]$ = 300 mmol/l (see Table 1).

Table 3. Effect of Al/Ti and Si/Ti molar ratios on the concentration of reduced titanium in the activated catalyst after the interaction of catalyst **2** with $AlEt_3$/DCPDMS

Experiment no.	Interaction conditions					[Ti]*, wt %	Fraction of Ti^{n+}, %	
	[Ti], mmol/l	[Al], mmol/l	Al/Ti, mol	[Si], mmol/l	Si/Ti, mol		Ti^{4+}	$Ti^{3+} + Ti^{2+}$
1	0.5	10	20	2.5	5	1.5	11	89
2	0.2	10	50	2.5	12.5	1.4	7	93
3	0.1	10	100	2.5	25	1.4	38	62
4	0.2	20	100	5	25	1.4	36	64
5**	0.2	20	100	0	0	1.7	9	91

Note: Interaction conditions: temperature, 70°C; time, 30 min.
* The total titanium content of the activated catalyst.
** The external donor was absent.

fraction of reduced titanium $[Ti^{2+} + Ti^{3+}]$ in the catalyst increased only slightly (from 78 to 83%; see experiments 1–3 in Table 2). In this case, a redistribution of reduced titanium species was observed: the fraction of Ti^{3+} ions decreased (to 62%), and the fraction of Ti^{2+} increased (to 21%). At all of the treatment temperatures of catalyst **1** with a mixture of $AlEt_3$/PTMS, the reduction of titanium was considerable but incomplete: the activated catalyst contained 17–22% Ti^{4+} ions (experiments 1–3). At the same time, upon the treatment of catalyst **1** with only $AlEt_3$ at the high molar ratio $AlEt_3$/Ti = 50, Ti^{4+} ions were reduced completely (experiment 4). The distribution of Ti^{n+} ions in catalyst **2** after the interaction with $AlEt_3$/DCPDMS at 50°C (experiment 5) was approximately the same as that in catalyst **1** treated with a mixture of $AlEt_3$/PTMS (experiment 2). As the temperature was increased to 70°C (experiment 6), the fraction of reduced titanium somewhat increased. Under all of the test conditions (temperature, 25–70°C; cocatalysts, $AlEt_3/D_2$ or $AlEt_3$; and Al/Ti ratio in the reaction mixture, 10 or 50), the predominance of titanium as Ti^{3+} ions was observed in the activated catalysts.

The amount of Ti^{3+} ions detected by EPR spectroscopy was 17–30% on a total titanium basis, which is much smaller than the value found by titration (62–78%). After the treatment of an activated catalyst with pyridine, the amount of Ti^{3+} ions measured by EPR spectroscopy noticeably increased (to 40–65%). Thus, as noted previously [8, 9], Ti^{3+} ions occur in two states in the activated catalyst: as isolated ions and as a constituent of surface associates with the predominance of these latter.

Table 3 demonstrates how the Al/Ti and Si/Ti molar ratios affect the degree of titanium reduction in catalyst **2** upon its interaction with $AlEt_3$/DCPDMS. As the Al/Ti ratio was increased as a result of a decrease in catalyst concentration (experiments 1–3), the fraction of reduced titanium changed from high (89 and 93% at Al/Ti ratios of 20 and 50 in the reaction mixture, respectively) to a much lower value (62% at Al/Ti = 100). If the Al/Ti ratio increased from 50 (experiment 2) to 100 because of an increase in the concentration of $AlEt_3$ (experiment 4), the fraction of

Table 4. Effect of the interaction time of catalyst **2** with $AlEt_3$/DCPDMS on the concentrations of various titanium ions in the activated catalyst

Experiment no.	Interaction time, min	Concentration			Concentration of Ti^{n+} (from the results of titration), %			Concentration of Ti^{3+} (according to EPR-spectroscopic data)**, %
		[Ti]*, wt %	[Al], wt %	Al/Ti, mol	Ti^{4+}	Ti^{3+}	Ti^{2+}	
1	10	1.6	1.5	1.7	32	68	0	45 (55)
2	30	1.4	1.3	1.65	35	65	0	–
3***	30	1.7	1.9	2.0	11	79	10	–
4	60	1.3	1.4	1.9	28	72	0	60 (55)

Note: Interaction conditions: temperature, 70°C; [Ti] = 0.2 mmol/l; $[AlEt_3]$ = 20 mmol/l; DCPDMS/Ti = 25.

* The total titanium content of the activated catalyst.

** The concentration of Ti^{3+} ions in the activated catalyst treated with pyridine is given in parentheses.

*** The catalyst was treated with only $AlEt_3$ (with no DCPDMS).

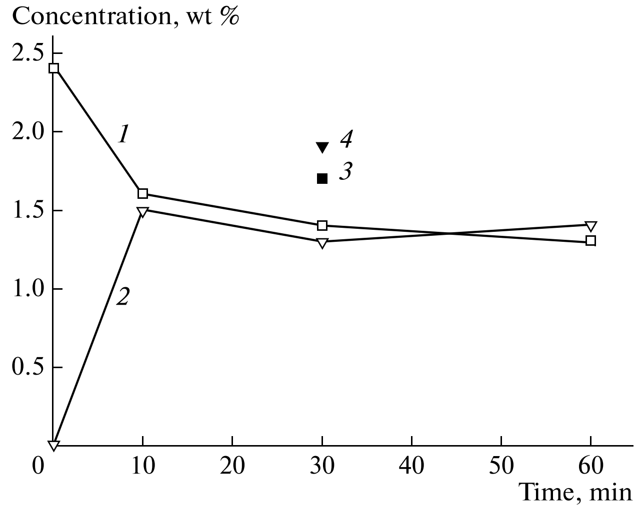
reduced titanium also became comparatively low (65%). In both cases, a decrease in the fraction of reduced titanium was observed at the highest molar ratio Si/Ti = 25. It is likely that the external donor at high values of Si/Ti restricts the possibility of titanium reduction as a result of the interaction of the catalyst with $AlEt_3$. In the absence of an external donor (experiment 5), the fraction of reduced titanium increased to 91% and approached a value that was reached at the ratios Si/Ti = 5 and 12.5 (experiments 1 and 2, respectively).

Table 4 and the figure contain data on the effect of the interaction time of catalyst **2** with the $AlEt_3$/DCPDMS cocatalyst on the concentrations of titanium and aluminum in the activated sample and on the distribution of titanium in various oxidation states in this sample. The interaction conditions were chosen so that the fraction of unreduced titanium remained noticeable and thereby more sensitive to the duration of treatment. Table 4 (experiments 1, 2, and 4) indicates that the fraction of Ti^{4+} under these conditions was 28–35%, and the fraction of Ti^{3+} was 65–72%. This distribution was reached even after 10 min, and it remained unchanged as the treatment time was increased to 60 min. In an individual experiment (experiment 3), we studied the interaction of the catalyst with only $AlEt_3$ with no external donor. In this case, the fraction of Ti^{4+} ions became noticeably smaller (11%) and a small amount of Ti^{2+} ions (10%) appeared.

Thus, the distribution of Ti^{n+} in the activated catalyst remained almost unchanged depending on the interaction time of the initial sample with the cocatalyst. The main fraction of titanium consisted of Ti^{3+} ions (65–72%). In the absence of an external donor, the fraction of Ti^{4+} ions decreased and Ti^{2+} ions were formed.

The figure shows data on changes in the total titanium and aluminum contents of activated catalysts depending on the duration of the interaction of initial catalyst **2** with $AlEt_3$/DCPDMS at 70°C. A dramatic decrease in the titanium content (from 2.4 to 1.6 wt %) and the appearance of aluminum (1.5 wt %) were noted within the first 10 min. The subsequent increase in the treatment time to 60 min did not result in a considerable change in the concentrations of titanium and aluminum. After the treatment of the initial catalyst with only $AlEt_3$, the concentrations of titanium and aluminum in the catalysts were higher than after the treatment with a mixture of $AlEt_3$ with DCPDMS. It is likely that the presence of DCPDMS as a cocatalyst constituent facilitated the removal of titanium from the catalyst and this donor competed with aluminum compounds for adsorption sites on the catalyst surface.

In catalyst **2** activated with a mixture of $AlEt_3$/DCPDMS at the ratio Si/Ti = 25, the concentrations of Ti^{3+} ions measured by EPR spectroscopy



Dependence of the concentrations of (*1*) titanium and (*2*) aluminum in the activated catalyst on the interaction time of initial catalyst **2** with the $AlEt_3$/DCPDMS cocatalyst. For comparison, points *3* and *4* are shown to indicate the concentrations of titanium and aluminum, respectively, in the activated catalyst after 30-min interaction of initial catalyst **2** with only $AlEt_3$ (with no external donor). The interaction conditions are specified in Table 4.

Table 5. Effect of the preliminary interaction between a catalyst and a cocatalyst on the rate of propylene polymerization

Experiment no.	Catalyst	Concentration, wt %		Average rate of polymerization	
		Ti	Al	(g PP) (g Cat)$^{-1}$ atm^{-1} h^{-1}	(g PP) (g Ti)$^{-1}$ atm^{-1} h^{-1}
1	**1**	2.0	–	900	45.0
2	Activated catalyst **1**	1.5	1.0	880	58.7
3	**2**	2.4	–	1430	59.6
4	Activated catalyst **2**	1.8	1.24	1370	76.1

Note: The catalysts were activated by treatment with the $AlEt_3$/PTMS cocatalyst at 50°C for 60 min; [Ti] = 0.75 mmol/l; [$AlEt_3$] = 7.5 mmol/l; [PTMS] = 0.75 mmol/l. Polymerization conditions: temperature, 70°C; pressure, 5 atm; duration, 2 h; [$AlEt_3$] = 4 mmol/l; Al/Ti = 300; Al/PTMS = 10; H_2 concentration in a gas phase, 2 vol %.

both without and with the use of pyridine treatment were close to the values found by titration (Table 4, experiments 1 and 4). Thus, the major portion of trivalent titanium in activated catalyst **2** occurred on the surface as isolated Ti^{3+} ions. Note that catalyst **2** differed from catalyst **1** in the coordination state of trivalent titanium. In the latter, mainly Ti^{3+} compounds occurred in an associated form and isolated Ti^{3+} ions occurred in a smaller amount (Table 2, experiments 1–3).

Effect of the Catalyst–Cocatalyst Preinteraction on the Rate of Propylene Polymerization

Table 5 summarizes data on the activities of initial and activated catalysts. Initial catalysts **1** and **2** (experiments 1 and 3) and corresponding activated catalysts (experiments 2 and 4), from which a portion of titanium compounds was removed as a result of treatment with a mixture of $AlEt_3$/PTMS, exhibited similar activities in the reaction of propylene polymerization per gram of catalyst. Because it is likely that soluble titanium compounds removed from the catalyst are inactive in this process, the activity of activated catalysts per gram of Ti was higher (experiments 2 and 4). Data on the morphology of PP particles suggest the absence of activity from soluble titanium compounds, which were formed upon the interaction of the catalyst with $AlEt_3$. If the soluble titanium compounds were active in the reaction, they would cause the formation of a powdered PP fraction. However, PP particles formed on the initial catalysts (experiments 1 and 3) did not contain a powdered fraction, and they were not different from PP particles on activated catalysts (experiments 2 and 4) in terms of morphology (particle size and shape and a narrow particle size distribution); their morphology repeated the morphology of catalyst particles.

Thus, the above study allowed us to make the following conclusions:

(1) The interaction of TMCs with a cocatalyst ($AlEt_3$ or $AlEt_3/D_2$) resulted in the reduction of tetravalent titanium and a transfer of a portion of titanium compounds into solution. In this case, different distributions of reduced titanium species in the activated catalyst and liquid phase were observed: Ti^{3+} and Ti^{2+} ions were predominant in the catalyst and liquid phase, respectively. Published data on the distribution of Ti^{n+} in the catalyst based on the analysis of the total reaction mixture (the activated catalyst together with the liquid phase) should be considered incorrect.

(2) The most significant decrease in the titanium content of a sample in the course of activation and the appearance of aluminum in activated catalysts were observed at 25°C, and a further increase in the temperature to 70°C did not cause considerable changes. The above changes occurred within the first 10 min of interaction, and an increase in the treatment time to 60 min had almost no effect on them. In the absence of an external donor, the concentrations of titanium and aluminum in the activated catalysts were higher. It is likely that the external donor (PTMS or DCPDMS) facilitated the removal of titanium compounds under the action of $AlEt_3$ and restricted the adsorption of aluminum compounds on the catalyst surface. For example, this can occur as a result of competitive adsorption at $MgCl_2$ sites, which became accessible after the removal of a portion of titanium compounds and internal donor D_1.

(3) The distribution of Ti^{n+} ions in activated catalysts depended on the conditions of catalyst interaction with a cocatalyst. The major portion consisted of Ti^{3+} ions (62–89%), whereas the remaining portion was either Ti^{4+} ions (22–35%) if the treatment was performed under comparatively mild conditions (temperature, 25°C; Si/Ti = 25) or Ti^{4+} (to 21%) and Ti^{2+} (9–21%) ions if the treatment conditions were more severe (temperature, 50 or 70°C; Si/Ti from 0 to 5). According to EPR-spectroscopic data, at the values of Si/Ti from 1 to 5, Ti^{3+} mainly occurred as associates or as isolated ions at Si/Ti = 25.

(4) The same rate of propylene polymerization per gram of catalyst was reached in the course of reaction on initial catalysts and activated catalysts with lower titanium contents than those of the initial ones. Therefore, titanium compounds removed from the catalyst upon interaction with $AlEt_3$ are inactive in the reaction of propylene polymerization.

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