INTRODUCTION

Supported titanium-magnesium catalysts (TMCs) are important as industrial catalysts in the polypropylene (PP) industry. Catalytic properties in stereospecific propylene polymerization are controlled by electron donor compounds, which are introduced in TMC’s during their preparation (internal donors, IDs) and by further electron donating compounds, introduced during the polymerization process (external donors, EDs). Despite numerous experimental [1-10] and theoretical [11-15] studies, many questions about the state of IDs and the changes taking place in the catalyst during the polymerization process are insufficiently clarified and are the subject of current research.

It is known that internal donors, such as benzoic, phthalic, succinic or malonic esters, are partially removed from the catalyst during polymerization, due...
to side reactions of the IDs with organoaluminum cocatalysts [16,17]. It is assumed that the external donor then occupies one vacant Lewis acid site on the surface of magnesium chloride catalyst near the active center and that this is essential for keeping the stereospecificity of the catalyst high during propylene polymerization. In previous studies, the decrease of activity of TMCs during polymerization was attributed to deactivation of active sites by their interaction with alkoxysilanes, used as external donors [7,17], or with an organoaluminum cocatalyst [17-20].

However, many details of this process remain unclear. The process of replacing an internal by an external donor occurs under polymerization conditions; this makes it difficult to obtain physical and chemical data about the changes taking place in the catalyst. IR spectroscopy, a simple and informative method for the study of heterogeneous catalysts, has been successfully applied to study the interaction of IDs such as ethylbenzoate (EB), dibutylphthalate (DBP) and others with MgCl$_2$ [1-7]. It was shown [2,5,9] that esters acting as IDs adsorb on the MgCl$_2$ surface by interaction of their carbonyl group with Lewis acid centers of the support. DRIFT spectra of ID/MgCl$_2$ samples allowed to identify several absorbance bands in the region 1630-1710 cm$^{-1}$ and to characterize stretching vibrations of carbonyl groups of adsorbed IDs on different faces of MgCl$_2$. DRIFT methods have also been used to study the process of catalyst formation of [1,2,3,7] and the interaction of TMCs with the cocatalyst AlEt$_3$ [5].

Previously, we have measured the basicity of a wide range of electron donor compounds, including those used for the preparation of TMCs [4]. It has thus been shown that the basicity of ethers and alkoxysilanes is higher than that of ketones and mono- and diesters, and that a stronger Lewis base, e.g. propyltrimethoxysilane (PTMS) can partially displace a weaker one (e.g. EB or DBP) from the surface of the magnesium chloride support.

In this work, we have studied, by chemical analysis and DRIFTS methods, the interaction of three types TMCs, prepared by different methods, with external donors (PTMS) under conditions closely similar to those prevailing during polymerization, in the presence and absence of an organoaluminum cocatalyst. Catalysts TMC-A and TMC-B were prepared using an MgCl$_2$ carrier obtained by reacting Mg with BuCl in heptane in the absence of electron donor compounds, and consecutive treatment of this MgCl$_2$ carrier with DBP and TiCl$_4$ and with (DBP·TiCl$_4$) complex, respectively. Catalyst TMC-C was synthesized by reacting TiCl$_4$ and DBP with Mg(OEt)$_2$ in chlorobenzene according to the procedure given in [21]. We also report on the activity of these catalysts for propylene polymerization under different reaction conditions. Based on the physico-chemical and catalytic data thus obtained, it is discussed which reactions of a TMC with an ED lead to changes in the activity of the catalyst and in the stereoregularity of polypropylene (PP).

**EXPERIMENTAL**

**Reagents**

All chemical reagents and solvents used in this study—heptane, chlorobenzene (PhCl) and dibutyl phthalate (DBP) were dried over molecular sieves. Heptane was additionally distilled under Na in an argon atmosphere, and chlorobenzene under P$_2$O$_5$ in an argon atmosphere.

Commercial titanium tetrachloride, propyltrimethoxysilane (PTMS) (from Aldrich) and Mg(OEt)$_2$ (from Aldrich, particle size of 0.5 mm) were used without additional purification. All chemicals were stored under an argon atmosphere.

**Synthesis of MgCl$_2$ (BuCl)**

An activated MgCl$_2$ sample was synthesized according to [5] and [22] by reaction of magnesium with BuCl (at a molar ratio of BuCl/Mg = 3) in n-heptane at 98°C, and then washed twice with the same solvent. MgCl$_2$(BuCl) sample (S$_{BET}$ = 70 m$^2$/g) contained ca. 10 wt% of organic products.

**Synthesis of DBP/MgCl$_2$**

A suspension of MgCl$_2$(BuCl) in chlorobenzene (PhCl) with concentration 40 g MgCl$_2$/1L chlorobenzene was treated with a solution of DBP in PhCl (CDBP = 0.2 M), at a molar ratio of DBP/MgCl$_2$ = 0.15 at 115°C for 1 h under a continuous flow of argon. After that, chlorobenzene was decanted and the sample was washed...
twice with hot (115°C) PhCl and three times with heptane at room temperature. The DBP/MgCl₂ sample contained 7.84 % wt of DBP

**Synthesis of TMC-A**

A suspension of MgCl₂(BuCl) in chlorobenzene with concentration 40 g MgCl₂/1L chlorobenzene was treated with a solution of DBP in PhCl (CDBP = 0.2 M), at a molar ratio of DBP/MgCl₂ = 0.15 at 115°C for 1 h under a continuous flow of argon. After that, chlorobenzene was decanted and the samples were washed twice with hot (115°C) PhCl and three times with heptane at room temperature. After that, chlorobenzene was decanted and the sample was washed twice with hot (115°C) PhCl and three times with heptane at room temperature. TMC-A catalyst contained 4.45% wt of DBP and 0.87% wt of Ti.

**Synthesis of TMC-B**

A suspension of MgCl₂(BuCl) in chlorobenzene with concentration 40 g MgCl₂/1L chlorobenzene was treated with a solution of complex (TiCl₄-DBP) in PhCl at a molar ratio of TiCl₄-DBP /MgCl₂ = 0.15 at 115°C for 1 h under a continuous flow of argon. After this reaction, chlorobenzene was decanted and the samples were washed twice with hot (115°C) PhCl and three times with heptane at room temperature. TMC-B catalyst contained 6.0% wt of DBP and 0.6% wt of Ti.

**Synthesis of TMC-C**

TMC-C catalyst was prepared by reacting Mg(OEt)₂ with TiCl₄ and DBP in a PhCl solution at a volume ratio of TiCl₄:PhCl = 1:1 and molar ratios of TiCl₄/Mg = 13 and DBP/Mg = 0.15 according to [21]. TMC-C catalyst contained 8.4% wt of DBP and 3.15% wt of Ti. The surface area (S_{BET}) was 275 m²/g.

**Treatment of TMC-A, TMC-B and TMC-C with heptane solution of PTMS**

A suspension of the respective catalyst, containing 40 g of catalyst/ 1L of heptane, was treated with a solution of PTMS in heptane at a molar ratio of Al/PTMS = 300 at 70°C for 1h under a continuous flow of argon. After that, heptane was decanted and the sample was washed three times with heptane at room temperature. The sample was then dried in vacuo and stored under an argon atmosphere.

**Treatment of TMC-A and TMC-C with heptane solution of AlEt₃**

A suspension of a catalyst, containing 40 g of catalyst/1L of heptane, was treated with a solution of AlEt₃ in heptane at a molar ratio of Al/Ti=300 at 70°C for 1h under a continuous flow of argon. After that, heptane was decanted and the sample was washed three times with heptane at room temperature. The sample was then dried in vacuo and stored under an argon atmosphere.

**Treatment of TMC-A and TMC-C with heptane solution of AlEt₃/PTMS**

A suspension of a catalyst, containing 40 g of catalyst/1L of heptane, was treated with a solution of AlEt₃/PTMS in heptane at molar ratios of Al/Ti = 300 and Ti/PTMS = 20 at 70°C for 1h under a continuous flow of argon. After that, heptane was decanted and the sample was washed three times with heptane at room temperature. The sample was then dried in vacuo and stored under an argon atmosphere.

**Chemical analysis**

The Si, Al and Ti contents of the samples were determined by atomic emission spectroscopy (ICP-AES) on an Optima 4300 DV (Perkin-Elmer) spectrometer, while the contents of DBP were determined by high-performance liquid chromatography (HPLC) in isocratic mode by using standard solutions of the compounds in acetonitrile. The measurements were made on a LC-20 Prominence (Shimadzu) liquid chromatograph.

**Polymerization of propylene**

Polymerization of propylene was carried out in a 0.7 L reactor in a heptane medium at 70°C under total pressure of 6 bar for 1 h: [AlEt₃] = 4 mmol/L; molar ratio of Al/PTMS = 10; catalyst loading = 0.03–0.04 g/L; and hydrogen content in the gas phase was 0.14 bar H₂. The stereospecificity of the catalyst was estimated from the content of atactic PP (APP), which was determined as the fraction of polymer dissolved in the...
Ziegler-Natta catalysts for propylene polymerization – Interaction of an external donor with the catalyst

heptane that was employed for polymerization.

FTIR measurements of samples
All operations were carried out in an inert Ar atmosphere. All samples were dried under vacuum to a residual pressure of $2 \times 10^{-2}$ mbar before measurements. Samples (0.2-0.3 g) were transferred, under an inert atmosphere, to a cuvette suitable for DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) measurements for FTIR characterization.

FTIR spectra were recorded with a FTIR-8300S Shimadzu spectrometer equipped with a DRS-8000 diffuse reflectance cell in the range of 400-6000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. All spectra are presented in form of Kubelka-Munk transformations (Eq. 1, where $R$ is the reflection):

$$F(R) = \frac{(1 - R)^2}{2 \cdot R}$$

RESULTS AND DISCUSSION

Composition of the initial catalysts TMC-A, TMC-B and TMC-C
Catalysts TMC-A and TMC-B were prepared on the same MgCl$_2$ carrier, but using different methods of adsorption of the active components DBP and TiCl$_4$. The total content of DBP and Ti is close to 340 µmol/g for catalysts TMC-A and TMC-B (Table 1, entries 2 and 6). However, the ratio of DBP/Ti in TMC-A (0.88) differs from that in TMC-B (1.76). It is probably due to the distinct synthesis method of these catalysts. Catalysts TMC-A was prepared via consecutive treatment of MgCl$_2$(BuCl) support by DBP and then TiCl$_4$. Catalyst TMC-B was prepared by the treatment of the same support by the complex (DBP∙TiCl$_4$). Catalyst TMC-C was prepared by treatment of the same support by the complex (DBP∙TiCl$_4$). It is known [9, 11] that DBP interacts effectively with the Lewis acid sites (LAS) of activated MgCl$_2$, i.e. with coordinatively unsaturated magnesium ions on the (110) and (104) faces. Results of theoretical calculations indicate the possibility of effective interaction of TiCl$_4$ mainly with four-coordinated magnesium ions on the (110) face [23]. Our results show that centers capable of effectively binding TiCl$_4$ remain after adsorption of DBP on the surface of MgCl$_2$. Presumably, part of the LAS remains unoccupied after the adsorption of DBP on the surface of activated magnesium chloride due to steric reasons [13]. The total content of TiCl$_4$ and DBP in catalyst TMC-C is about 2.8 times higher than that in catalysts TMC-A and TMC-B (Table 1, entries 2, 6, 9). The ratio of DBP/Ti = 0.5 for catalyst TMC-C is significantly lower than that for catalysts TMC-A and TMC-B, for which this value is 0.88 and 1.76, respectively. So, the synthesis method of the catalyst determines fixation of TiCl$_4$ and the internal donor DBP. Introduction of TiCl$_4$ and DBP into TMC-C during synthesis of the catalyst results in the higher content of these compounds in TMC-C since the formation of magnesium chloride occurs in the presence of TiCl$_4$ and DBP [21]. We can assume that this is the main cause of the higher content of TiCl$_4$ and DBP. In addition, MgCl$_2$ with lower surface area ($S_{BET}$ of 80 m$^2$/g) and larger crystallite size (15 nm in (110) direction) was used for the preparation of TMC-A and TMC-B, while the MgCl$_2$ support for TMC-C has a mesoporous structure with higher surface area ($S_{BET}$ of 275 -300 m$^2$/g) and a small crystallite size (5.5 nm in (110) direction) [21].

Interaction of catalysts TMC-A, TMC-B and TMC-C with PTMS, AlEt$_3$ and AEt$_3$/PTMS
We have studied the interaction of TMCs with PTMS in heptane suspension at 70°C, at a ratio of PTMS/ID = 20. These conditions are very close to those prevailing during the polymerization reaction. It is found that 58.8% of DBP is removed from the catalyst TMC-A under these conditions (Table 1, entries 2 and 3) but the titanium content is only slightly reduced. At the same time, a significant quantity of PTMS (232 µmol/g) is adsorbed on the catalyst. The total content of the components DBP+PTMS+TiCl$_4$ in the catalyst (467 µmol/g) is significantly higher than the content of DBP+TiCl$_4$ before treatment with PTMS (341 µmol/g). Probably, PTMS displaces mainly DBP from the surface of MgCl$_2$ and is also adsorbed on the surface of titanium compounds. Similar changes were observed in the catalyst TMC-B. The quantity of DBP is reduced by 43.5%, while the titanium concentration remains practically unchanged (Table 1, entries 6,7). The total content of the components DBP+PTMS+TiCl$_4$ (409 µmol/g) exceeds the content
of DBP+TiCl₄ in the initial catalyst (339 µmol/g).

The results of the interaction of TMC-C with PTMS differ from the data for the catalysts TMC-A and TMC-B. The DBP and Ti content in the catalyst TMC-C is slightly reduced after treatment with a heptane solution of PTMS (by 12.9 and by 19.8% mol for DBP and Ti, respectively, Table 1, entries 9, 10). The adsorbed PTMS content for TMC-C (103 µmol/g) is significantly lower than for TMC-A and TMC-B (232 and 170 µmol/g, respectively, Table 1, entries 3,7,10). For catalyst TMC-C the total content of the components DBP+PTMS+TiCl₄ does not exceed the content of DBP+TiCl₄ in the initial catalyst (Table 1, entries 9, 10). This indicates that in this case there is only a partial replacement of TiCl₄ and DBP by the external donor.

Thus, the amount of removed DBP and adsorbed PTMS and the molar ratio of DBP/Ti in the catalysts before and after treatment of PTMS depend on the synthesis method of the catalyst. Particularly the amounts of removed DBP and adsorbed PTMS after treatment with PTMS alone decrease in the order of TMC-A > TMC-B > TMC-C. PTMS displaces DBP due to its high basicity (ΔH₄ binder = -99.4 and -63.9 kJ/mol for PTMS and DBP, respectively [4]).

The ratio DBP/Ti in the initial catalysts increases in the order: TMC-C (0.46) < TMC-A (0.88) < TMC-B (1.76). This ratio decreases sharply after a treatment of the catalysts TMC-A and TMC-B with an external donor (0.39 and 1.04, respectively), but remains practically constant in the catalyst TMC-C. This indicates that the synthesis method of the catalyst affects the nature of the interaction of MgCl₂ with DBP and TiCl₄. The internal donor (DBP) is probably more strongly linked to MgCl₂ in the TMC-C catalyst.

The total content of DBP+PTMS in the catalysts TMC-A, TMC-B and TMC-C after treatment with PTMS or PTMS/AlEt₃ at 70°C during 1 h.

<table>
<thead>
<tr>
<th>Additional treatment of catalyst</th>
<th>Content, µmol/g</th>
<th>Percentage of extracted compound, % mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiCl₄</td>
<td>DBP</td>
</tr>
<tr>
<td>MgCl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>TMC-A</td>
<td>2</td>
<td>181</td>
</tr>
<tr>
<td>3 PTMS</td>
<td>169</td>
<td>66</td>
</tr>
<tr>
<td>4 AlEt₃</td>
<td>115</td>
<td>10</td>
</tr>
<tr>
<td>5 PTMS/AlEt₃</td>
<td>123</td>
<td>10</td>
</tr>
<tr>
<td>TMC-B</td>
<td>6</td>
<td>123</td>
</tr>
<tr>
<td>7 PTMS</td>
<td>117</td>
<td>122</td>
</tr>
<tr>
<td>8 PTMS/AlEt₃</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>TMC-C</td>
<td>9</td>
<td>657</td>
</tr>
<tr>
<td>10 PTMS</td>
<td>527</td>
<td>263</td>
</tr>
<tr>
<td>11 AlEt₃</td>
<td>460</td>
<td>100</td>
</tr>
<tr>
<td>12 PTMS/AlEt₃</td>
<td>497</td>
<td>162</td>
</tr>
</tbody>
</table>

*- D = DBP + PTMS
adsorbed on the surface of the catalyst (57 and 285 µmol/g, respectively, Table 1, entries 2, 5). Similar changes were observed for the catalyst TMC-B (Table 1, entries 6, 8).

In the case of TMC-C, the DBP and Ti contents decrease also after treatment with PTMS/AIE₃ solution, but to a lesser degree (by 46.4 and 24.4%). PTMS and AIE₃ appear in the catalyst (197 and 382 µmol/g, respectively, Table 1, entries 9, 12). The (Ti+DBP+Si+Al) content (1235 µmol/g) exceeds the (Ti+DBP) content (959 µmol/g) in the initial catalyst. Probably, part of the Al compound is bound to Ti centers in the catalyst TMC-C when it is treated with PTMS/AIE₃ solution.

The molar ratio of DBP/TiCl₄ differs significantly in the catalysts TMC-A, TMC-B and TMC-C after this treatment (0.08, 0.14 and 0.33, respectively). These data indicate that in the case of TMC-C the internal donor (DBP) is more strongly bound to MgCl₂.

The total content of DBP+PTMS (359 µmol/g) is much higher for the TMC-C treated with PTMS/AIE₃ in comparison with the TMC-A catalyst (67 µmol/g). But the molar ratio of (DBP+PTMS)/Ti is approximately similar for both catalysts (0.72 and 0.55).

Therefore, the synthesis method of the catalyst determines the resulting interaction of the catalyst with the external donor (PTMS), with AIE₃ and with PTMS/AIE₃.

**DRIFTS data on the interaction of catalysts TMC-A, TMC-B and TMC-C with PTMS, AIE₃ and AIE₃/PTMS**

The interaction of DBP and DIBP with MgCl₂ and the state of DBP in DBP/MgCl₂ and in TMCs have been studied by DRIFTS [1-7]. It was shown [2,3] that a set of surface DBP compounds, characterized by two narrow bands of the ortho-disubstituted benzene ring of DBP at 1592 and 1580 cm⁻¹ and a broad band in the region 1630-1710 cm⁻¹, was formed on the MgCl₂ carrier and on TMCs. Similar results were obtained in the present study for the catalysts studied, which were obtained by different methods (Figure 1). At the same time, some differences are observed for catalysts TMC-B and TMC-C as compared with catalyst TMC-A. In addition to the bands in the region of 1630-1710 cm⁻¹, there are additional bands in the region 1710-1850 cm⁻¹, which characterize PhC(O)Cl, adsorbed on MgCl₂, in the spectra of these TMCs. Formation of PhC(O)Cl during the synthesis of various TMCs has been attributed to a side reaction between DBP and TiCl₄ [2].

In the DRIFT spectrum of TMC-C, there are mainly absorbance bands at 1657 and 1710 cm⁻¹, while there are mainly absorbance bands at 1680 and 1710 cm⁻¹ in the spectra of TMC-A and TMC-B (Figure 1, spectra 2-4). It should be noted that the carbonyl group stretching vibrations of the catalysts investigated are similar to those of the carrier DBP/MgCl₂.

Since the catalyst TMC-B was obtained by adsorption of the complex (DBP·TiCl₄), one might assume that the complex (DBP·TiCl₄) adsorbed onto the surface of catalyst TMC-B gave rise to the band with νC=O = 1670 cm⁻¹ (Figure 1, spectra 3, 5). But since low-frequency bands at 1640-1680 cm⁻¹ are also present in the spectrum of DBP/MgCl₂ (Figure 1, spectrum 1), bands in the region 1640-1680 cm⁻¹ cannot be uniquely attributed to the adsorbed complex DBP·TiCl₄ on the surface of the magnesium chloride. Probably, a part of the (DBP·TiCl₄) complex dissociates during the synthesis of the TMC-B catalyst while some part stays intact.

By quantum-chemical calculations it has been shown that phthalates might adsorb on mononuclear Ti³⁺ centers on the (110) face to form complex I [14, 23]. The binding energy of this complexe (20.1 kcal/mol) was calculated to be close to the heat of adsorption of phthalates on the (110) face of magnesium chloride.
In line with this proposal, complex I is characterized by a νC=O vibration at 1660-1690 cm⁻¹ that is similar to the νC=O band of phthalate adsorbed on magnesium chloride (1650-1700 cm⁻¹).

Figure 2 shows the IR spectra of the catalyst TMC-B before and after its treatment with a solution of PTMS in the region of C=O stretching vibrations. A broad asymmetric absorbance band in the region 1650-1720 cm⁻¹ with a maximum at 1680 cm⁻¹ characterizes the C=O stretching vibrations of adsorbed DBP in the spectrum of catalyst TMC-B (Figure 2, spectrum 1). The spectrum can be deconvoluted into three absorbance bands at 1654, 1680 and 1715 cm⁻¹.

After treatment of the catalyst with a solution of PTMS its spectrum becomes more symmetric (Figure 2, spectrum 2). Deconvolution of the spectrum in the region 1620-1750 cm⁻¹ now yields two absorbance bands at 1675 and 1705 cm⁻¹, while the intensity of the absorbance bands in the region 1710-1850 cm⁻¹ decreases. Two new absorbance bands at 1190 and 1220 cm⁻¹ characterize the stretching vibrations of the C-O-Si groups of PTMS adsorbed on MgCl₂.

DRIFT spectra of TMC-C before and after treatment with PTMS are shown in Figure 3. A broad line in the region 1630-1720 cm⁻¹ and absorbance bands in the region of 1720-1850 cm⁻¹ are observed in the initial spectrum of catalyst TMC-C (Figure 1, spectrum 1). The band in the region 1630-1720 cm⁻¹ narrows and its maximum shifts to higher frequencies after treatment of TMC-C with PTMS (Figure 3, spectrum 2), while the intensity of the bands in the region 1710-1850 cm⁻¹ decreases sharply. A deconvolution of the spectra into its components in the 1620-1750 cm⁻¹ region yields three absorbance bands at 1650, 1675 and 1705 cm⁻¹ in the original catalyst TMC-C, while only two absorbance bands at 1675 and 1705 cm⁻¹ are observed after treatment of the catalyst with PTMS.

When the catalysts TMC-B and TMC-C were treated with a solution of AlEt₃/PTMS at 70°C for one hour, their IR spectra changed dramatically. No stretching vibrations in the C=O region were observed in the spectrum of catalyst TMC-B (spectrum in Figure 2 not shown). This DRIFTS result agrees with the chemical analysis data (Table 1) which show that after this treatment, almost the whole of DBP (95 mol%) is removed from the catalyst.

After treatment of the catalyst TMC-C with a solution of AlEt₃/PTMS, the intensity of absorbance bands in the C=O region decreases (Figure 3, spectrum 4). The deconvolution of the spectrum into its components in the 1600-1750 cm⁻¹ region singles out three absorbance bands at 1650, 1675 and 1700 cm⁻¹. Of these absorbance bands, the one at 1700 cm⁻¹ has the highest intensity. This means that predominantly one type of surface DBP compounds, adsorbed on MgCl₂, remains on the catalyst surface after treatment with a solution of AlEt₃/PTMS.

Similar changes were observed in the spectra of the TMC-B and TMC-C in the case of their treatment with AlEt₃. No stretching vibrations in the C=O region are observed in the spectrum of catalyst TMC-B, but a low-intensity, broad absorbance band in the region 1600-1750 cm⁻¹ is observed in the catalyst TMC-C (Figure 3, spectrum 3).
The DRIFT-spectroscopic results agree well with our chemical analysis data, according to which treatment of the catalysts with a heptane solution of AlEt$_3$/PTMS at 70°C leads to strong changes in the chemical composition of the catalysts (Table 1), which indicate a selective removal of parts of the DBP from the catalyst surface.

DRIFTS data show mainly one type of adsorbed DBP remains on the TMC-C surface since the absorbance band at 1700 cm$^{-1}$ is the most intense in the spectrum of TMC-C after treatment with AlEt$_3$/PTMS.

DFT calculations had shown that coordination of two alkoxy silane molecules (Me$_2$Si(OMe)$_2$) to a four-coordinate exposed Mg ion on the MgCl$_2$ (110) plane caused this surface site to become preferred over the MgCl$_2$ (104) surface site with only a single donor per exposed Mg [29]. In accordance with this study, we can propose that the (110) face is similarly preferred for PTMS during the treatment of TMC-C with AlEt$_3$/PTMS.

### Propylene polymerization

Catalysts TMC-A and TMC-C, before and after treatment with PTMS, were tested for their activity in propylene polymerization at different polymerization conditions: (1) in the presence of AlEt$_3$ and in the absence of PTMS; (2) in the presence of an external donor (PTMS) and AlEt$_3$; (3) after treating the catalyst with the external donor (PTMS) in the reactor during 1 h and at 70°C, propylene, hydrogen and AlEt$_3$ were introduced to the reactor. Catalyst activities and properties of the resulting PP are shown in Table 2. The initial TMC-A and TMC-C catalysts have different activities per g of catalyst due to the large differences in the process of preparation, their chemical composition, and their specific surface areas (Table 2, entries 1, 5). The titanium content is much higher in the catalyst TMC-C and therefore, the polymerization activity per gram of catalyst is about 5 times higher in the

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**Table 2. Activities of catalysts TMC-A and TMC-C for propylene polymerization (70°C, propene pressure 6 bar, hydrogen pressure 0.14 bar, reaction time 1 h).**

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>Activity</th>
<th>APP$^{(4)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kgPP/gCat⋅h</td>
<td>kgPP/mmolTi⋅h</td>
</tr>
<tr>
<td>1</td>
<td>TMC-A</td>
<td>2.1</td>
<td>11.7</td>
</tr>
<tr>
<td>2</td>
<td>TMC-A/PTMS</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>TMC-A</td>
<td>0.4</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>TMC-A</td>
<td>1.3</td>
<td>8.4</td>
</tr>
<tr>
<td>5</td>
<td>TMC-C</td>
<td>9.9</td>
<td>15.1</td>
</tr>
<tr>
<td>6</td>
<td>TMC-C/PTMS</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>7</td>
<td>TMC-C</td>
<td>1.7</td>
<td>5.5</td>
</tr>
<tr>
<td>8</td>
<td>TMC-C</td>
<td>7.2</td>
<td>11.0</td>
</tr>
</tbody>
</table>

$^{(1)}$ [AlEt$_3$]=0.004 mmol/ml, [Al]/[Ti]=300, without PTMS

$^{(2)}$ Catalyst, PTMS at molar ratio Ti/PTMS=20 and hexane (250 mL) were added to a 1L autoclave. The suspension was stirred during 1 h at 70°C. Thereafter, propylene, hydrogen and AlEt$_3$ (0.004 mmol/ml, [Al]/[Ti]=300) were introduced to the autoclave.

$^{(3)}$ [AlEt$_3$]=0.004 mmol/ml, [Al]/[Ti]=300 and Al/PTMS=10

$^{(4)}$ amount of PP dissolved in heptane
case of TMC-C than for the catalyst TMC-A. The PP obtained using catalyst TMC-C has a lower content of atactic fractions. This is probably due to the higher DBP/Ti ratio in TMC-C than in TMC-A after the treatment with AlEt₃ (Table 1, entries 4, 11).

Pretreatment of TMC-A and TMC-C catalysts with PTMS leads to a sharp activity decrease, by a factor of about 25 (Table 2, runs 1 and 2, 5 and 6). These data indicate that pretreatment of the catalyst with PTMS results in deactivation of active sites, probably by adsorption of PTMS to Ti ions. Our chemical analysis data show indeed that the high contents of PTMS and of total PTMS+DBP+Ti components can be explained only by an adsorption of PTMS on Ti centers of the catalyst (Table 1, runs 3, 10).

We carried out additional experiments, in which catalysts TMC-A and TMC-C were treated with PTMS directly in the reactor at 70°C for 1h, before starting the propylene polymerization (Table 2, entries 1 and 3, 5 and 7).

In this case, the activity of the catalysts was also found to be reduced, but to a lesser extent, while the fraction of atactic polypropene (APP) decreased approximately twice. This means that PTMS is absorbed mainly on non-stereospecific catalyst sites and deactivates them.

Further experiments were carried out with catalysts TMC-A and TMC-C under conditions typical for the stereospecific polymerization of propylene. In this case, a heptane solution of AlEt₃ (molar ratio Al/Si = 20) was injected into the reactor before starting the polymerization (Table 2, entries 1 and 4, 5 and 8). The activity of both catalysts decreased slightly and the yield of atactic PP was greatly reduced in this case.

Thus, the conditions of interaction of an external donor (PTMS) with TMCs significantly affect the composition of these catalyst systems and their properties in propylene polymerization. The presence of the AlEt₃ cocatalyst in the reaction system is the most important factor controlling the interaction of a TMC with the external donor (PTMS). If the AlEt₃ cocatalyst is absent in the reaction system, the external donor PTMS partially replaces DBP on the surface of MgCl₂ and is mainly adsorbed on coordinatively unsaturated Ti ions; this leads to deactivation of active sites and, hence, to a great decrease in activity. In the presence of AlEt₃, however, reaction between AlEt₃ and an ID such as DBP results in freeing LAS on the surface of MgCl₂. As a consequence, the external donor PTMS is mainly adsorbed onto free acidic sites of MgCl₂ and on coordinatively unsaturated Ti ions, predominantly on non-stereospecific active sites, thus resulting in some decrease of activity and in a marked increase in stereospecificity.

So polymerization data show:

- The activity of both catalysts was found to decrease sharply (5-6 fold) after a pretreatment with PTMS. Probably, PTMS is firmly adsorbed on the titanium ions, leading to a sharp decrease in the activity;
- When treated only with the cocatalyst AlEt₃, the catalysts showed high activity and low stereospecificity. Reduced stereospecificity is in this case related to the removal of DBP from the catalysts;
- Their activity decreases only slightly if polymerization proceeds with a mixture AlEt₃/PTMS, but in this case the amount of atactic PP decreases;
- The differences in activity and stereospecificity of the TMC-A and TMC-C catalysts are probably due to different ratios of the individual components (Ti, DBP, PTMS, Al) in the initial state of these catalysts and after the reaction with a mixture of AlEt₃/PTMS.

**CONCLUSION**

Three types of TMC were used in this study. Catalysts TMC-A and TMC-B were prepared using an MgCl₂ carrier obtained by reacting Mg with BuCl in heptane in the absence of electron donor compounds, and consecutive treatment of this MgCl₂ carrier with DBP and TiCl₄ and with (DBP-TiCl₄) complex, respectively. Catalyst TMC-C was synthesized by reacting TiCl₄ and DBP with Mg(OEt)₂ in chlorobenzene. The interaction of TMCs prepared by different procedures with the external donor PTMS, AlEt₃ and a mixture of PTMS/AlEt₃ was studied by chemical analysis and infrared diffuse reflectance spectroscopy (DRIFTS).

It was found the amount of DBP and TiCl₄ removed from the catalysts after a treatment with PTMS or a mixture PTMS/AlEt₃ depended on: (i) a method of the catalyst preparation; (ii) a chemical composition and
textural parameters of the initial TMC; (iii) a presence of AlEt₃ at the interaction of TMC with an external donor.

DRIFTS and chemical composition data showed that PTMS could substitute both TiCl₄ and DBP. DRIFTS data evidenced also selective substitution of DBP by PTMS. One type of adsorbed DBP remained mainly after treatment of TMC with PTMS/AlEt₃ mixture.

The presence of AlEt₃ in the PTMS/AlEt₃ mixture played a key role on the chemical composition of the catalysts (content and DBP/TiCl₄ ratio). The treatment of the catalysts with PTMS alone before polymerization led to a sharp decrease of activity due to its adsorption on titanium species, while the interaction of the catalysts with the PTMS/AlEt₃ mixture led only to a slight decrease of activity, probably due to a deactivation of non-stereospecific active species.

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