

Supported Titanium–Magnesium Catalysts for Propylene Polymerization

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Abstract—The results of studies of the synthesis and properties of supported titanium–magnesium catalysts for propylene polymerization performed at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, are considered. The composition of the catalysts is $\text{TiCl}_4/\text{D}_1/\text{MgCl}_2\text{--AlEt}_3/\text{D}_2$, where D_1 and D_2 are stereoregulating donors. With the use of the procedure proposed for the synthesis of titanium–magnesium catalysts, the morphology of catalyst particles depends on the stage of the preparation of a Mg-containing support. The titanium–magnesium catalysts developed afforded polypropylene (PP) in a high yield; this PP was characterized by high isotacticity and excellent morphology. The controllable fragmentation of the catalyst by the polymer is of crucial importance for the retention of the morphology of titanium–magnesium catalyst particles in PP. The fragmentation of catalyst particles to microparticles occurred in the formation of more than 100 g of PP per gram of the catalyst. The surface complexes were studied by DRIFT and MAS NMR spectroscopy and chemical analysis. It was shown that the role of internal donors is to regulate the distribution of TiCl_4 on different MgCl_2 faces and, thereby, to influence the properties of PP. It was found that chlorine-containing complexes of aluminum compounds were formed on the catalyst surface by the interaction of the catalyst with AlEt_3 ; these complexes can block the major portion of titanium chloride. Data on the number of active sites and the rate constants of polymer chain propagation (k_p) at various sites indicate that donor D_1 increases the stereospecificity of the catalyst because of an increase in the fraction of highly stereospecific active sites, at which k_p is much higher than that at low-stereospecificity active sites. Donor D_2 enhances the role of D_1 . Similar values of k_p at sites with the same stereospecificity in titanium–magnesium catalysts and TiCl_3 suggest that the role of the support mainly consists in an increase in the dispersity of titanium chloride.

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INTRODUCTION

Polypropylene (PP) is a large-scale polymer, and its production is rapidly developing (by 5–6% annually). In 2010, the world consumption of PP will be greater than 50 million tons. Montecatini (Italy) started the commercial manufacture of PP 50 years ago. Titanium trichloride of the $\text{TiCl}_3\text{--AA}$ type (violet modification), which was prepared by the reduction of TiCl_4 with aluminum metal and then activated by dry grinding in a ball mill, served as a catalyst [1]. The grinding resulted in an uncontrollable morphology of PP particles.

In 1972, Solvay considerably improved catalysts based on TiCl_3 . The brown modification of $\beta\text{-TiCl}_3$, which was prepared by the reduction of TiCl_4 with AlEt_2Cl , was specially treated with diisoamyl ether followed by thermal treatment in the presence of an excess of TiCl_4 [2]. The three-step synthesis of this catalyst was subsequently simplified to a two- or single-step synthesis. The second generation of TiCl_3 catalysts (Solvay type) exhibited a higher (by a factor of 3–5) activity and higher stereospecificity (96–98 against 90–92%) and allowed one to control the morphology of PP particles. One of these second-generation catalysts, which was developed at the Boreskov Institute of Catal-

ysis, has been successfully used in the manufacture of PP at OOO Tomskneftekhim [3].

In the manufacture of PP, AlEt_2Cl is used as a cocatalyst with TiCl_3 . The replacement of AlEt_2Cl by AlEt_3 improved the activity of the catalyst but decreased its stereospecificity and dramatically increased the fraction of low-stereoregularity PP. The slurry polymerization of propylene in heptane or hexane requires the washing of PP with alcohols to remove TiCl_3 and AlEt_2Cl residues and the separation of a soluble low-stereoregularity PP fraction (usually referred to as atactic PP) from a hydrocarbon solvent. Correspondingly, the stages of solvent regeneration and PP powder drying for the removal of a hydrocarbon solvent should be involved in the process. To simplify the PP production technology, highly active catalysts that do not require the removal of catalyst residues from the polymer were necessary. Supported catalysts with a much lower content (by one order of magnitude) of an active component (titanium chloride) could meet these requirements. A long search resulted in finding MgCl_2 as the most efficient support [1, 4]. On the one hand, this support has a crystal lattice similar to the lattice of TiCl_3 (this is important for the formation of active sites with the required properties). On the other hand, it is not hydro-

lyzed with the release of corrosive HCl in contact with the atmosphere. Trialkylaluminum (AlEt_3 or $\text{Al}(i\text{-Bu})_3$) is used as a cocatalyst for these catalysts in place of AlEt_2Cl ; this allows one to exclude the subsequent stage of chlorine removal from the polymer.

In this paper, we consider the results of recent studies performed at the Boreskov Institute of Catalysis concerning the synthesis of titanium–magnesium catalysts for propylene polymerization, the replication and fragmentation of the catalyst with the polymer, the characterization of surface complexes in titanium–magnesium catalysts, and the determination of the number of active sites and the propagation rate constants on sites with different stereospecificity.

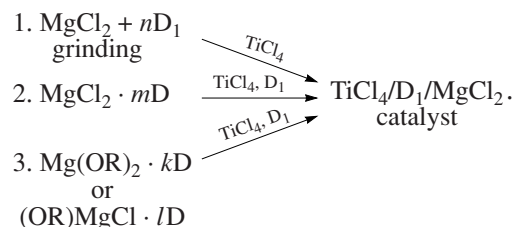
Synthesis of Supported Titanium–Magnesium Catalysts

The first $\text{TiCl}_4/\text{MgCl}_2\text{--AlR}_3$ supported catalysts were developed in the late 1960s for ethylene polymerization. Note that only the use of “activated” MgCl_2 with a minimum crystallite size as a support (for example, it was prepared by grinding [5–7]) provided high activity of supported titanium–magnesium catalysts. However, they exhibited low stereospecificity in the process of propylene polymerization. The introduction of stereoregulating additives into the solid catalyst composition (internal donor D_1) and an organoaluminum cocatalyst (external donor D_2) made it possible to develop the $\text{TiCl}_4/\text{D}_1/\text{MgCl}_2\text{--AlR}_3/\text{D}_2$ catalytic system suitable for propylene polymerization in the 1970s [8]. In this system, aromatic acid esters such as ethyl benzoate and ethyl anisate or ethyl toluate are used as donors D_1 and D_2 , respectively. These catalysts, which are referred to as third-generation catalysts, exhibit high activity and do not require PP washing with alcohols. However, their stereospecificity (92%) is insufficiently high. More recently, donors that are more efficient were found, namely, 1,2-diester of aromatic acids, in particular, phthalates as D_1 and alkoxysilanes (phenyltriethoxy-, alkyltrimethoxy-, and dialkyldimethoxysilanes) as D_2 [9]. These fourth-generation catalysts exhibit high stereospecificity (>96%), and their activity in the course of polymerization is more stable. The use of fourth-generation catalysts made it possible to perform modern efficient PP production processes in a liquid propylene medium and in a gas phase without the stages of washing polymer powder to remove catalyst residues and the atactic PP fraction and removing the hydrocarbon solvent by drying.

The subsequent studies resulted in the appearance of internal donors D_1 that provided high stereospecificity of titanium–magnesium catalysts without the use of external donor D_2 . These are 1,3-diethers (such as 2,2-diisobutyl-1,3-dimethoxypropane) [10]. Catalysts with these donors, which exhibit higher activity, are sometimes referred to as fifth-generation catalysts.

The procedures for the synthesis of titanium–magnesium catalysts, which have been described in many

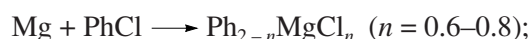
patents, can be combined into the following three main groups (D is a donor):



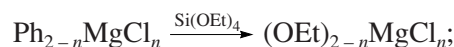
Many catalysts exhibit high activity and stereospecificity; however, in addition to these parameters, the morphology of catalyst particles is a very important characteristic of polymerization catalysts. The morphology of catalyst particles is responsible for the morphology of the resulting PP. The first of the above groups of procedures for the synthesis of titanium–magnesium catalysts does not allow one to control the morphology of catalyst particles. In the second group, titanium–magnesium catalysts are synthesized from the solutions of MgCl_2 complexes (D = alcohols, phosphates, etc.). In this case, the morphology of particles depends on the precipitation conditions of complexes both as a result of the interaction of MgCl_2 complexes with TiCl_4 (e.g., see [11]) and before the interaction with TiCl_4 (e.g., see [12]). In the third group of procedures, catalyst particles are formed simultaneously with the in situ formation of MgCl_2 ; as a rule, these catalysts exhibit the highest activity. With the use of a solid magnesium alkoxide, the morphology of catalyst particles depends on the morphology of parent support particles (e.g., see [13]), so that special procedures should be developed for regulating the morphology of the magnesium alkoxide. In a number of cases, the Mg-containing support particles with a controlled morphology are formed from magnesium alkoxide solutions (with a titanium alkoxide, alcohols, etc.) before the interaction with TiCl_4 (e.g., see [14]). In the synthesis of catalysts from magnesium alkoxy chlorides, which are prepared, for example, by the interaction of alkyl Grignard compounds with alcohols or alkoxysilanes [15], the Mg-containing support particles are usually formed previously; subsequently, they interact with TiCl_4 .

The synthesis of a catalyst for propylene polymerization with the use of a soluble organomagnesium compound as a starting component was developed at the Boreskov Institute of Catalysis [16]. This synthesis is performed in the following three steps:

(1) preparation of an organomagnesium compound



(2) preparation of the support



(3) preparation of the catalyst



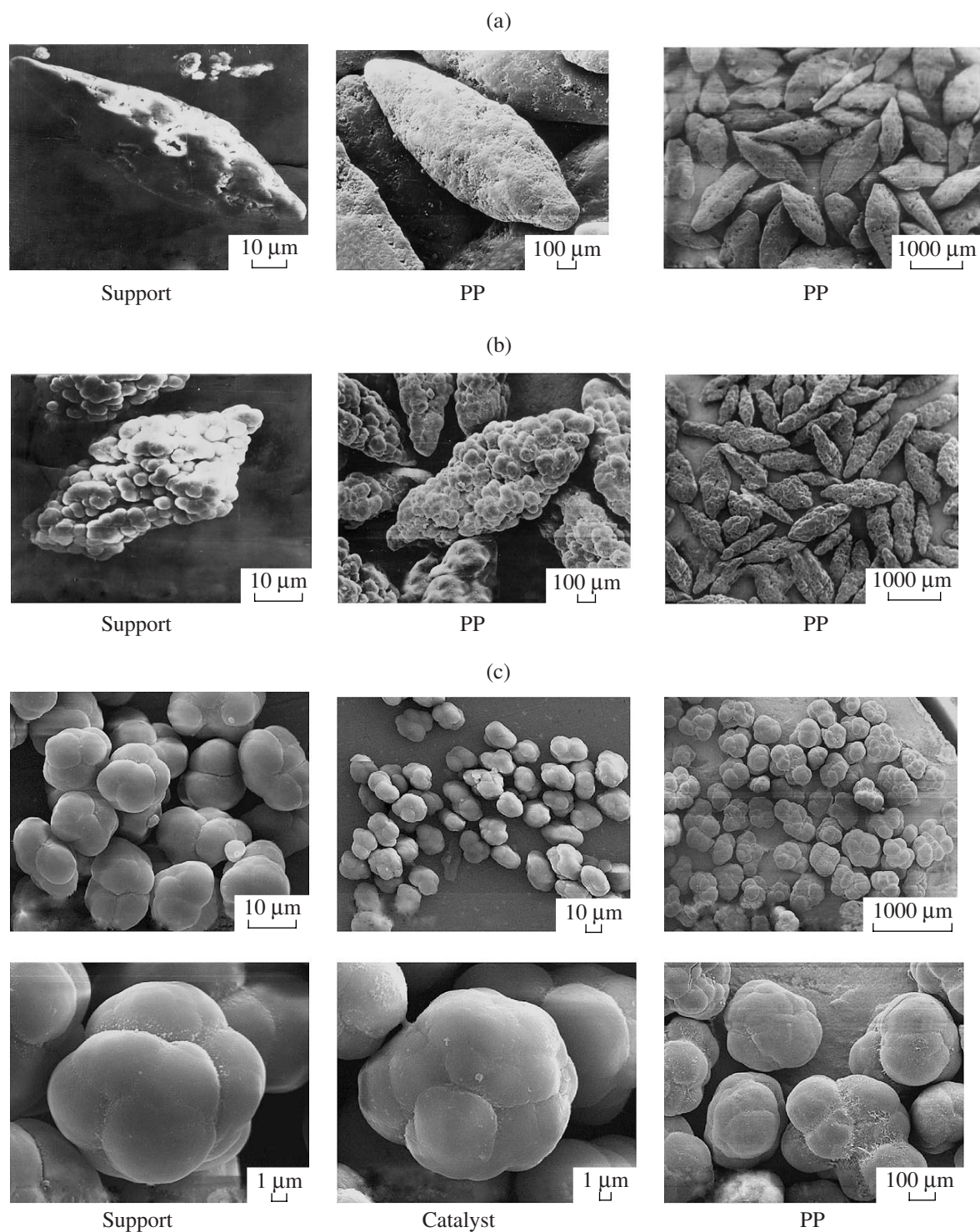


Fig. 1. SEM micrographs of support, catalyst, and PP particles different in the morphology of particles depending on support synthesis conditions: (a) elongated particles without a pronounced substructure, (b) elongated particles with a pronounced substructure, and (c) round particles.

The morphology of catalyst particles and, correspondingly, PP particles is determined at the stage of support synthesis. This is demonstrated in Fig. 1a, which shows that an unusual (elongated) shape of sup-

port particles is reproduced in polymer particles. This can be seen even more clearly in Fig. 1b, where the substructure of support particles is reproduced in polymer particles. The morphology of catalyst particles can be

Effect of prepolymerization on the properties of a titanium–magnesium catalyst in propylene polymerization

Experiment no.	Amount of prepolymer, g _{PP} /g _{Cat}	Average rate of polymerization, g _{PP} g _{Cat} ⁻¹ h ⁻¹	Atactic PP*, %	Bulk density of PP powder, g/l	SPAN**
1	0	7600	6.0	210	1.45
2	1	6100	0.8	470	0.35
3***	200	6500	0.6	490	0.36

Note: The prepolymerization of propylene was performed at 30°C by varying the amount of propylene. The main process was performed in heptane at 70°C and 7 bar for 1.5–2 h. [AlEt₃] = 5 mmol/l; PrSi(OMe)₂/Al = 20; average size of catalyst particles, 20 μm (SPAN < 0.5).

* The fraction of PP soluble in heptane in the course of polymerization.

** SPAN = (d₉₀ – d₁₀)/d₅₀, where d₁₀, d₅₀, and d₉₀ are the particle sizes in the integrated distribution curve (Fig. 2) at the points that correspond to PP fractions of 10, 50, and 90 wt %, respectively.

*** In experiment 3, the catalyst was introduced into the reaction medium at 30°C and 1 bar (instead of 70°C and 7 bar in experiments 1 and 2); then, the temperature and pressure were increased to 70°C and 7 bar, respectively.

controlled by varying the conditions of support synthesis. Based on a study of the synthesis of a support and a catalyst, an IK-8-21 catalyst was developed for propylene polymerization. The yield of PP on this catalyst was higher than 1000 kg/(g Ti), and the isotacticity was higher than 97%. The product exhibited an excellent morphology: these were dense spherical PP particles (the bulk density was higher than 450 g/l) with a narrow particle-size distribution without a dust fraction (Fig. 1c). The average particle size of a catalyst for propylene polymerization can be regulated over the range of 10–50 μm.

Catalyst Replication and Fragmentation by a Polymer

The control of the morphology of PP particles is based on the well-known replication phenomenon, that is, the formation of a polymer particle on a catalyst particle with the reproduction of its shape [17]. In this case, not only the shape but also the morphology (substructure) of catalyst particles are reproduced [18]. The fragmentation of a catalyst particle by the polymer formed on catalyst microparticles occurs in the course of polymerization.

To retain the effect of replication, the initial polymerization conditions are of considerable importance. If the catalyst is introduced into a reactor under severe near-industrial conditions (70°C and 7 bar), catalyst macroparticles can undergo partial or complete degradation as a result of a dramatic growth of PP particles with the formation of a loose polymer or a dust fraction, respectively. This catalyst fragmentation with the loss of the replication effect is an uncontrollable process. If polymerization is preliminarily performed on a catalyst under mild conditions (30°C and 1–2 bar) and then the catalyst is introduced into a reactor, which operates under industrial conditions, dense polymer particles are formed. The morphology of these particles replicates the morphology of catalyst particles. The fragmentation of catalyst macroparticles with the retention of the replication effect can be considered as a controllable process.

These conclusions were supported by data given in the table and Figs. 2 and 3. Depending on whether the catalyst particles are immediately introduced into a reaction medium at 70°C and 7 bar (experiment 1) or the prepolymerization initially occurs on them under mild conditions (experiments 2 and 3), PP particles with dramatically different morphologies are formed. It is believed that, because of the cocrystallization of polymer chains and the action of adhesion forces, the prepolymer (formed at a lower rate at the stage of prepolymerization) cements catalyst particles sufficiently strongly for the particle morphology to remain unaffected in the polymerization zone under severe conditions.

Even small prepolymer amounts retain the morphology of catalyst particles. Thus, even at a prepolymer/catalyst weight ratio of 1 : 1 (table, Fig. 3, experiment 2), PP particles retained the morphology of the catalyst, just as in the case of higher ratios (experiment 3).

Fraction of PP particles, wt %

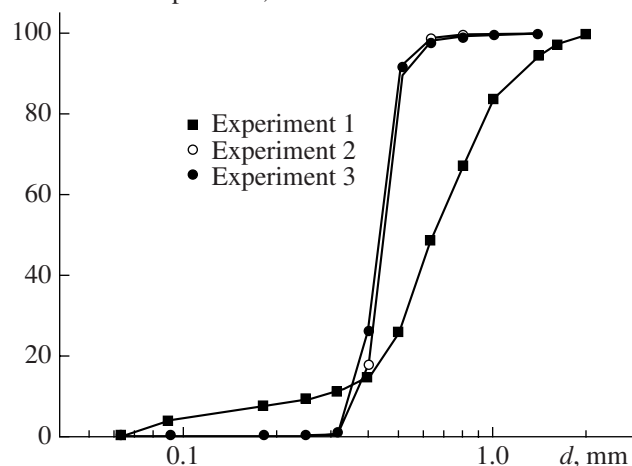


Fig. 2. Particle-size distribution of PP (based on sieve analysis data). See the table for experimental details.

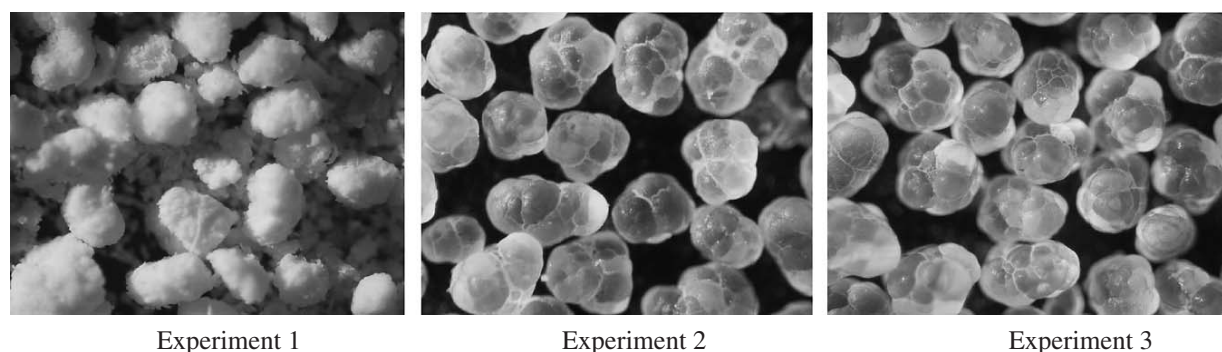


Fig. 3. Optical photographs of PP particles (see the table for experimental details).

It was of interest to find how rapidly the catalyst with a particle size of 10–50 μm was fragmented by the polymer to a microparticle size of several tens of nanometers. For this estimation, we used data on the rate of ethylene polymerization. The dense catalyst particles used in the manufacture of PP exhibited very low activity in ethylene polymerization [19]. This was explained by diffusion limitations on ethylene; these limitations resulted in a very low ethylene concentration within the catalyst macroparticle because of the high reactivity of active sites toward ethylene polymerization. As a consequence, ethylene polymerization occurred mainly on the outer surface of a macroparticle. Therefore, the macroparticle was fragmented by polyethylene (PE) much more slowly than by PP.

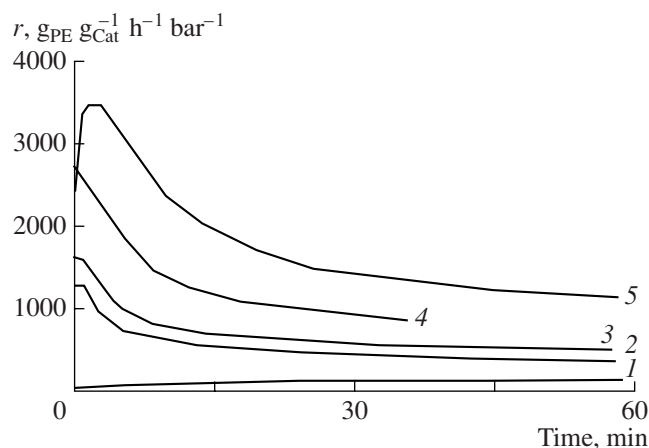


Fig. 4. Dependence of the rate of ethylene polymerization on the time of reaction on catalysts after propylene prepolymerization at C_3H_6 /catalyst weight ratios of (1) 0, (2) 70, (3) 140, (4) 280, and (5) 420. The prepolymerization of propylene was performed at 30°C for 10 min and then at 70°C for 15 min; thereafter, C_3H_6 was removed. We assumed that 30% of the introduced propylene was prepolymerized. Ethylene polymerization conditions: temperature, 70°C; C_2H_4 pressure, 2 bar; catalyst, TiCl_4 /dibutyl phthalate/ MgCl_2 (2 wt % Ti); $[\text{AlEt}_3] = 5 \text{ mmol/l}$.

The catalyst prefragmentation by PP has a strong effect on the rate of ethylene polymerization (Fig. 4). The rate of ethylene polymerization considerably increased with the propylene/catalyst ratio at the stage of prepolymerization. The maximum rate of ethylene polymerization at the beginning of polymerization increased by a factor of ~ 30 , as compared with the polymerization rate on the initial catalyst (without propylene prepolymerization). We believe that this effect was due to the decrease in the diffusion limitations on ethylene as a result of the controlled fragmentation of a catalyst particle by PP. Our previous data [20] indicate that the considerable increase in the overall rate of ethylene polymerization (r_{PE}) was due to the increase (by a factor of 2) in the number of active sites (C_p) and the significant increase (by a factor of 10) in the rate of polymerization on single active sites (r_{PE}/C_p value). The r_{PE}/C_p ratio is determined by the rate constant of polymer chain propagation (k_p) and the concentration of ethylene near the active site. Because k_p is a constant, it is reasonable to assume that the concentration of ethylene near the active site increases dramatically with an increasing prePP/catalyst ratio.

Note that the rate of ethylene polymerization noticeably decreased in the course of the reaction (Fig. 4). It was likely due to the deactivation of active sites and/or a decrease in the concentration of ethylene within a macroparticle as the PE/prePP ratio increased because of differences in the solubility and the rate constants of diffusion of ethylene in PE and PP.

Thus, the controllable fragmentation of the catalyst by PP was much more effective than by PE. The maximum effect of catalyst fragmentation was reached upon the formation of more than 100 $\text{g}_{\text{PP}}/\text{g}_{\text{Cat}}$. The controllable fragmentation dramatically increased the activity of catalysts in the reaction of ethylene polymerization because of a considerable decrease in diffusion limitations on ethylene.

Composition of the Surface Compounds in Supported Titanium–Magnesium Catalysts

In the course of catalyst synthesis, TiCl_4 and electron-donating compounds (internal donors), which are responsible for the high stereospecificity of catalysts, interact with the surface reaction sites of activated MgCl_2 . In this case, TiCl_4 and the donor interact with MgCl_2 independently of one another to form stable surface complexes, which cannot be removed by catalyst washing with hydrocarbon solvents [21–23]. These surface compounds are formed in the interaction with coordinatively unsaturated magnesium ions in MgCl_2 at the lateral faces (100) and (110) of magnesium chloride [24]. To understand the mechanism of stereoregulation and to control the catalytic properties of these systems, it is very important to find the manner in which TiCl_4 and the donor are distributed over the support surface and the active sites are constructed.

To study surface compounds formed in titanium–magnesium catalysts, we used model catalysts prepared by the adsorption of stereoregulating electron-donating compounds and TiCl_4 on a support of finely divided MgCl_2 [25, 26]. We measured the adsorption capacities of this support for TiCl_4 and a donor (ethyl benzoate, dialkyl phthalate, or succinate), which were supported either individually or in combination. We used diffuse reflectance IR spectroscopy to study the distribution of a donor over the surface of MgCl_2 . The donor forms three main complexes **A**, **B**, and **C** on the surface of MgCl_2 ; the stretching frequencies of the carbonyl group at 1650–1652, 1669–1675, and 1695–1699 cm^{-1} correspond to these complexes, respectively (Fig. 5a). It is most likely that these complexes are formed by the interaction of the donor with the surface ions of Mg in various chlorine environments at the magnesium chloride faces (100) (complex **C**) and (110) (complexes **A** and **B**). The major portion of ethyl benzoate occurred as a constituent of complex **B** ($\nu_{\text{C=O}} = 1675 \text{ cm}^{-1}$). If the donors were phthalates (diethyl phthalate, dibutyl phthalate, and diisobutyl phthalate) or succinate, carbonyl groups were distributed between complexes of different types in approximately the same manner: 45–50% of the donors were a constituent of complex **C**, and complexes **A** and **B** contained 10–20% each.

We studied the donor distribution over the surface of MgCl_2 using diffuse reflectance IR spectroscopy in both the absence and the presence of TiCl_4 . This study allowed us to estimate the distribution of TiCl_4 on the support surface. TiCl_4 partially replaced donors in complexes **A**–**C** and converted a portion of them into acid chlorides (Fig. 5b). We measured the amounts of adsorbed TiCl_4 on the support surface (based on the replaced donor amount) and the donor/ TiCl_4 ratio for each particular site **A**, **B**, and **C**. In a catalyst with ethyl benzoate, the major portion of TiCl_4 occurred at sites **B** and **C** [25, 26]. As for ethyl benzoate, more than 70% of this compound occurred in complexes **B**, whereas it was practically absent from complexes **C**. For sites **A**

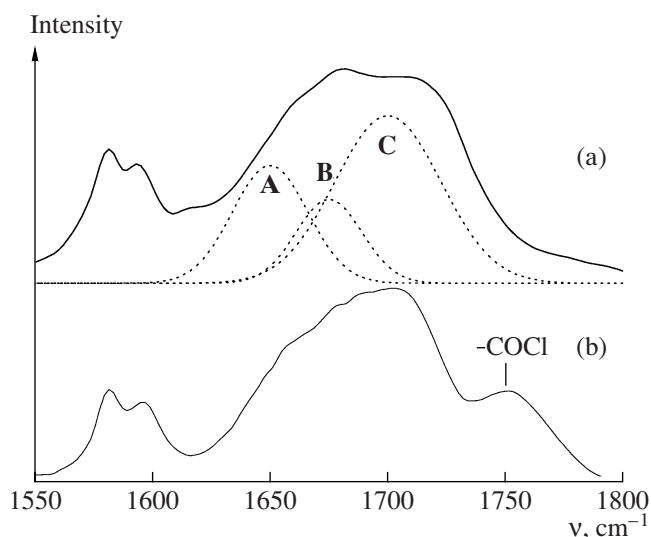


Fig. 5. Diffuse reflectance IR spectra of diethyl phthalate adsorbed on MgCl_2 in the region of the stretching vibrations of carbonyl groups (a) in the absence and (b) in the presence of TiCl_4 .

and **B**, the ethyl benzoate/ TiCl_4 molar ratio was (1.2–1.8) : 1. This means that ethyl benzoate molecules were adsorbed on the surface of MgCl_2 near the molecules of TiCl_4 , and they could affect the properties of active sites. In catalysts with phthalates, the concentrations of TiCl_4 and the donor/ TiCl_4 ratios on sites **A**, **B**, and **C** were similar [25, 26]. With the use of succinate, which has two carbonyl groups (as well as phthalate), as a donor, a dramatically different distribution of TiCl_4 was observed: as compared with phthalate catalysts, the amount of TiCl_4 on sites **C** increased, whereas the amounts on sites **A** and **B** somewhat decreased [26]. The succinate/ TiCl_4 ratios on different sites were also dramatically different from the phthalate/ TiCl_4 ratios. This ratio in complexes **A** and **C** was much lower, whereas it reached a maximum in complexes **B**. Note that such a low donor/ TiCl_4 ratio in complexes **C** and a maximum value in complex **B** were also observed in a study of a catalyst containing ethyl benzoate.

It is well known that PPs prepared on titanium–magnesium catalysts with various internal donors are characterized by different molecular-weight distributions. In particular, the molecular-weight distribution of PP prepared on titanium–magnesium catalysts containing ethyl benzoate or succinate was broader than that of PP prepared on catalysts containing dialkyl phthalates. Our experimental data suggest that the effect of an internal donor on the distribution of TiCl_4 is responsible for the formation of PP with a broadened molecular-weight distribution on titanium–magnesium catalysts containing ethyl benzoate and succinate.

The active sites of titanium–magnesium catalysts were formed by the interaction of the catalyst with an organoaluminum cocatalyst (usually, AlEt_3). The cocat-

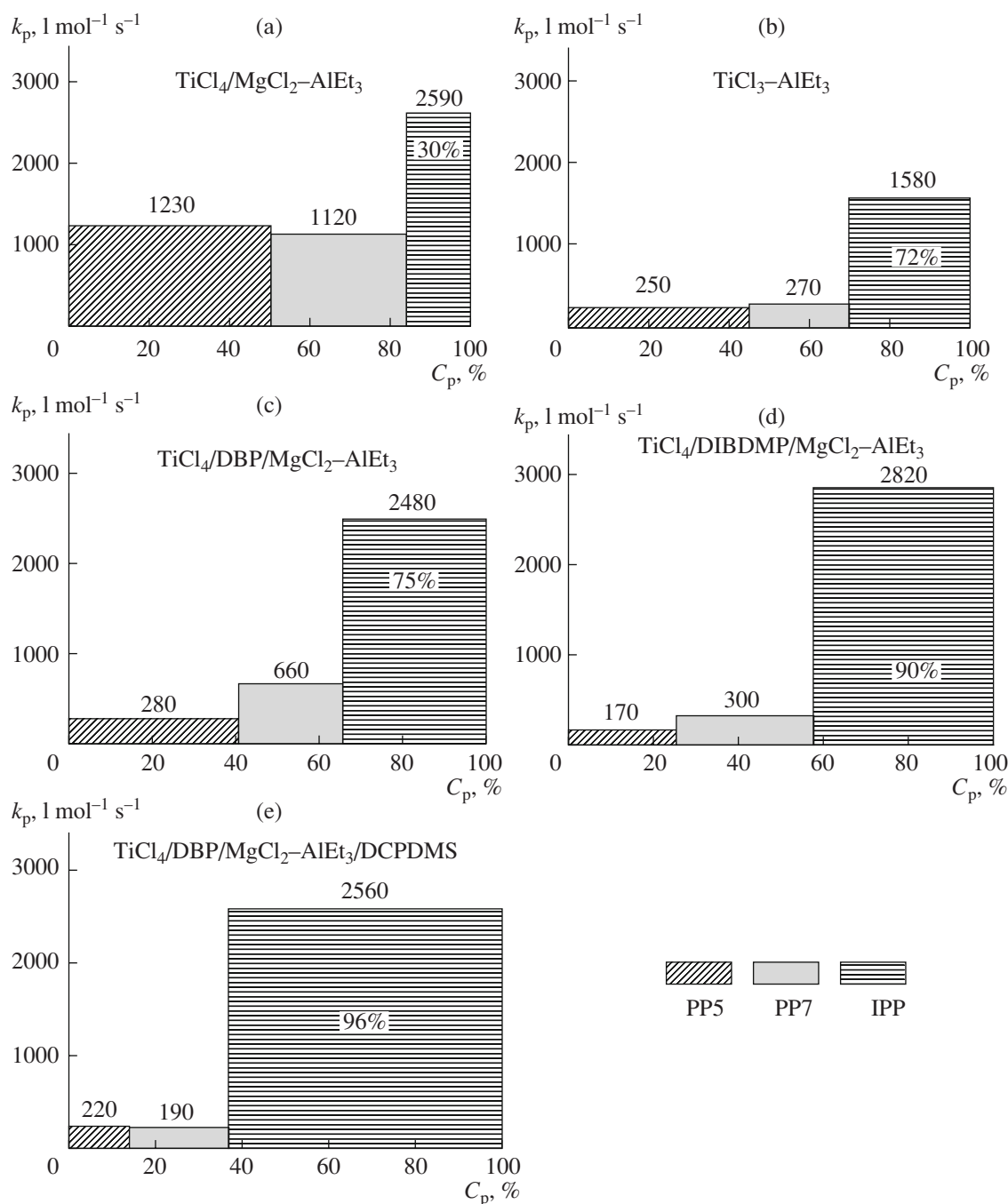


Fig. 6. Proportions of PP fractions obtained on active sites possessing different stereospecificities and characterized by different k_p values for different catalytic systems: (a) catalyst without a stereoregulating donor, (b) conventional TiCl_3 catalyst, (c, d) catalysts with internal stereoregulating donors, and (e) catalyst with internal and external stereoregulating donor. DBP = dibutyl phthalate; DIBDMP = 2,2-diisobutyl-1,3-dimethoxypropane; DCPDMS = dicyclopentylmethoxysilane; PP5 and PP7 are the polypropylene fractions successively soluble in boiling pentane and boiling heptane, respectively; IPP = fraction insoluble in boiling heptane.

alyst alkylated and reduced supported TiCl_4 and removed a considerable portion of an internal donor from the catalyst, whereas aluminum compounds were strongly adsorbed on the surface [4, 27]. To maintain the high stereospecificity of a catalyst, an external donor (such as alkoxysilane) was used with the cocatalyst; this external donor occupied surface sites that

became free after the removal of the internal donor. As we found previously using MAS ^{13}C NMR spectroscopy [28], aluminum mainly occurred as dialkylaluminum chloride on the catalyst surface; dialkylaluminum chloride formed several complexes with various coordination environments of aluminum atoms. The relative fraction of these complexes depended on the conditions

of the interaction of the catalyst and the cocatalyst. In the presence of an external donor, the concentration of aluminum compounds on the catalyst surface decreased because of competition between AlEt_2Cl and this external donor for surface sites released after the removal of the internal donor by the cocatalyst [29]. In this case, the external donor had no effect on the ratio between different complexes with the participation of aluminum compounds. Only a fraction of chlorine-containing aluminum compounds was removed under the action of trialkylaluminum. Therefore, the fraction of titanium ions in the active state depended on the adsorption and desorption of chlorine-containing aluminum compounds, which blocked active sites. This fact can explain the necessity of the use of an excess of trialkylaluminum in polymerization and the low efficiency of AlEt_2Cl as a cocatalyst.

Effect of Donors on the Activity and Stereospecificity of Supported Catalysts

We obtained data on the number of active sites and the propagation rate constants at sites with different stereospecificity using the ^{14}CO inhibition of propylene polymerization on various titanium–magnesium catalysts with and without internal and external donors [19, 20]. Figure 6 shows data on k_p and the fraction of active sites with different stereospecificity for various catalysts. The active sites were subdivided into nonstereospecific sites, which formed an atactic PP fraction (fraction PP5); low-stereospecificity sites, which formed a stereoblock fraction (fraction PP7); and stereospecific sites, which formed an isotactic PP fraction (fraction IPP). The ratio between various PP fractions depended on both the fraction of corresponding active sites in the total number of active sites and the value of k_p , which characterizes sites with a particular stereospecificity. In a supported catalyst containing no stereoregulating donors, the fraction of stereospecific active sites was very low (~16%, Fig. 6a). The introduction of an internal donor considerably decreased the value of k_p on nonstereospecific active sites and noticeably increased the fraction of stereospecific active sites (to 34% with the use of dibutyl phthalate (Fig. 6c) and to 43% with the use of diisobutyldimethoxypropane (Fig. 6d)). The introduction of an external donor resulted in a further increase in the fraction of stereospecific active sites (to 63%, Fig. 6e). In all cases, the value of k_p on stereospecific active sites remained almost constant and much higher than k_p on nonstereospecific and low-stereospecificity active sites. The total number of active sites remained almost unchanged upon the introduction of an external donor (~23 mmol/(mol Ti), Figs. 6c, 6e). An increase in the catalyst activity upon the introduction of an external donor was due to an increase in the fraction of stereospecific active sites at which k_p was much higher than that on

nonstereospecific active sites. The experimental data suggest that the introduction of an external donor resulted in the formation of stereospecific active sites in place of a portion of nonstereospecific active sites.

It was of interest to compare these results with data on a traditional TiCl_3 catalyst (Fig. 6b). In terms of the values of C_p and k_p , which correspond to different PP fractions, TiCl_3 was most similar to the $\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$ catalyst (Fig. 6c). In both cases, the constants k_p on stereospecific sites were much higher (by a factor of 6–9) than those on nonstereospecific active sites. At the same time, the corresponding values of k_p on these two catalysts differed by no more than a factor of 2. This fact suggests a similarity between the compositions and structures of corresponding active sites, as well as that the MgCl_2 support affected the number of active sites (increased the dispersity of titanium chloride) with no changes in the reactivity of these sites.

REFERENCES

- Galli, P. and Haylock, J.C., *Prog. Polym. Sci.*, 1991, vol. 16, p. 443.
- German Patent 2213086, 1972.
- Bukatov, G.D., Sergeev, S.A., Zakharov, V.A., Tolstov, G.P., Postoev, A.G., Kuznetsov, V.L., Tikhonov, I.B., Korolev, S.V., and Maier, E.A., *Plast. Massy*, 2004, no. 5, p. 9.
- Barbe, P.C., Cecchin, G., and Noristi, L., *Adv. Polym. Sci.*, 1987, vol. 81, p. 1.
- Kashiwa, N., *Polym. J.*, 1980, vol. 12, p. 603.
- Galli, P., Barbe, P., Guidetti, G., Zannetti, R., Martorana, A., Marigo, A., Bergozza, M., and Fichera, A., *Eur. Polym. J.*, 1983, vol. 19, p. 19.
- Zakharov, V.A., Perkovets, D.V., and Bukatov, G.D., *Kinet. Katal.*, 1988, vol. 23, p. 1202.
- German Patent 2 643 143, 1977.
- Patent 0 045 977 EP, 1982.
- Albizzati, E., Giannini, U., Morini, G., Galimberti, M., Barino, L., and Scordamaglia, R., *Macromol. Symp.*, 1995, vol. 89, p. 73.
- UK Patent 2111066, 1983.
- US Patent 4298718, 1981.
- US Patent 4535068, 1985.
- US Patent 5077357, 1991.
- Patent 0319227 EP, 1989.
- RF Patent 2152404, 2000; 2191196, 2002.
- Boor, J., Jr., *Ziegler-Natta Catalysts and Polymerizations*, New York: Academic, 1979, p. 180.
- Bukatov, G.D., Zaikovskii, V.I., Zakharov, V.A., Kryukova, G.N., Fenelonov, V.B., and Zagafskaya, R.V., *Vysokomol. Soedin., Ser. A.*, 1982, vol. 24, p. 542.
- Zakharov, V.A., Bukatov, G.D., and Barabanov, A.A., *Macromol. Symp.*, 2004, vol. 213, p. 19.

20. Bukatov, G.D., Zakharov, V.A., and Barabanov, A.A., *Kinet. Katal.*, 2005, vol. 46, no. 2, p. 180 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 2, p. 166].
21. Terano, M., Kataoka, T., and Keii, T., in *Catalytic Polymerization of Olefins*, Keii, T. and Soga, K., Eds., Amsterdam: Kodansha-Elsevier, 1986, p. 407.
22. Sergeev, S.A., Bukatov, G.D., Zakharov, V.A., and Moroz, E.M., *Makromol. Chem.*, 1983, vol. 184, p. 2421.
23. Sormunen, P., Hjertberg, T., and Iiskola, E., *Makromol. Chem.*, 1990, vol. 191, p. 2663.
24. Busico, V., Corradini, P., DeMartino, L., Proto, A., Savino, V., and Albizzati, E., *Makromol. Chem.*, 1985, vol. 186, p. 1279.
25. Potapov, A.G., Bukatov, G.D., and Zakharov, V.A., *J. Mol. Catal. A: Chem.*, 2006, vol. 246, p. 248.
26. Potapov, A.G., Zakharov, V.A., and Bukatov, G.D., *Kinet. Katal.*, 2007, vol. 48, no. 3, p. 426 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 3, p. 403].
27. Noristi, L., Barbe, P.C., and Baruzzi, G., *Makromol. Chem.*, 1991, vol. 192, p. 1115.
28. Potapov, A.G., Terskikh, V.V., Zakharov, V.A., and Bukatov, G.D., *J. Mol. Catal. A: Chem.*, 1999, vol. 145, p. 147.
29. Potapov, A.G., Terskikh, V.V., Bukatov, G.D., and Zakharov, V.A., *J. Mol. Catal. A: Chem.*, 2000, vol. 158, p. 457.