DRIFTS study of the interaction of the internal donor in TiCl$_4$/di-n-butyl phthalate/MgCl$_2$ catalysts with AlEt$_3$ cocatalyst

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ABSTRACT

The interaction of di-n-butyl phthalate (DBP as the internal donor) with AlEt$_3$ cocatalyst was studied by DRIFT spectroscopy for the DBP/MgCl$_2$ sample and supported TiCl$_4$/DBP/MgCl$_2$ catalysts. For DBP/MgCl$_2$ sample, it was shown that AlEt$_3$ partially removes all types of DBP complexes from the MgCl$_2$ surface and adsorbs on surface sites released by the removal of DBP. In the case of supported catalysts, the cocatalyst predominantly removes more weak DBP complexes. In addition, the cocatalyst completely removes loosely coordinated DBP and surface complexes of phthaloyl chlorides formed at the catalyst preparation. A part of removed DBP can adsorb again on the catalyst surface as complexes with surface alkylaluminum chloride compounds. The external donor alkylalkoxysilane does not markedly influence the removal of DBP complexes from the catalyst surface.

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1. Introduction

High stereospecificity of supported titanium–magnesium catalysts of propylene polymerization is determined by stereo-regulating electron-donor compounds used both at preparation of catalysts ("internal donor") and at polymerization ("external donor") [1–3]. Numerous works were performed to study a composition of the catalysts and state and distribution of donors and TiCl$_4$ complexes on the surface of the catalysts [4–16]. A lot of investigations were focused to study the interaction of the catalysts with organoaluminum cocatalyst [17–29]. In particular, it was shown that larger part of internal donor is removed from the catalysts by a cocatalyst (trialkylaluminium) and that resulted in marked decrease of the stereospecificity of the catalysts [17,19–25]. To keep a performance of the catalysts, external donors are additionally used in polymerization. These donors most likely occupy, on the surface of the catalysts, the sites released by the removal of internal donors. The data on changes of internal donors in catalysts during its interaction with cocatalyst are limited [28,29]. Particularly, recently we obtained such data for supported titanium–magnesium catalyst containing ethyl benzoate (EB) as the internal donor [30].

The most known internal donors in modern titanium–magnesium catalysts are dialkylphthalates, particularly di-n-butylphthalate (DBP). Earlier we demonstrated that DBP forms several types of complexes with surface-exposed magnesium ions

of the MgCl$_2$ support or the catalyst [12]. These complexes are identified by IR-spectroscopy by positions of carbonyl bands of DBP. In the present study we used IR-spectroscopy of diffuse reflectance (DRIFTS) to study the interaction of the DBP/MgCl$_2$ sample and the TiCl$_4$/DBP/MgCl$_2$ catalysts with AlEt$_3$ cocatalyst. Two catalysts were studied: (i) the model catalyst prepared by the interaction of TiCl$_4$ and DBP with highly dispersed MgCl$_2$; (ii) the catalyst, similar to a commercial one, prepared by the interaction of TiCl$_4$ and DBP with Mg(OEt)$_2$. In the last case, the formation of the support (MgCl$_2$) took place during the catalyst preparation via chlorination of Mg(OEt)$_2$ by TiCl$_4$. The use of these two catalysts allows us to extend the data for model samples to real catalysts and to compare these data for diester DBP with our data for monoester EB [30].

2. Experimental

2.1. Materials

Heptane, n-butylchloride, chlorobenzene (PhCl), DBP were used after dehydration over molecular sieves. All the preparation and manipulation with the samples were performed under argon atmosphere. Argon gas was dried with molecular sieves and a Drierite gas drying unit with anhydrous calcium sulfate.

2.2. Support

The highly dispersed MgCl$_2$ support was prepared via the interaction of magnesium metal powder with C$_4$H$_9$Cl (molar ratio C$_4$H$_9$Cl/Mg = 3) in heptane at 98 °C with subsequent washing with

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heptane. The resulting $MgCl_2$ support contained ca. 5 wt.% of organic residue and had the surface area of ca. 100 m^2/g.

2.3. Preparation of samples

The DBP/$MgCl_2$ sample (6.5 wt.% of DBP (250 μmol/g $MgCl_2$)) was prepared by addition of DBP to a suspension of $MgCl_2$ (DBP/$MgCl_2$ = 0.07) in PhCl (25 ml/g of $MgCl_2$) at 115 °C and keeping the reaction mixture at this temperature for 1 h. The resulted sample was washed once with PhCl at 115 °C and twice with heptane.

Titanium–magnesium catalyst (I) with a composition of $TiCl_4$/DBP/$MgCl_2$ (0.82 wt.% of Ti (180 μmol/g $MgCl_2$), 2.8 wt.% of DBP (120 μmol/g $MgCl_2$ as the sum with phthaloyl chlorides)) was prepared via treatment of the highly dispersed $MgCl_2$ support with a mixture of $TiCl_4$/PhCl (1:1 vol., Ti/Mg = 10) in the presence of DBP (DBP/Mg = 0.07) at 115 °C for 1 h and followed by two treatments with the same $TiCl_4$/PhCl mixture at 115 °C for 1 h and 0.5 h.

Titanium–magnesium catalyst (II) with a composition of $TiCl_4$/DBP/$MgCl_2$ (1.92 wt.% of Ti (495 μmol/g $MgCl_2$), 10.5 wt.% of DBP (485 μmol/g $MgCl_2$ as the sum with phthaloyl chlorides)) was prepared via treatment of $Mg(OEt)_2$ (Aldrich grade) with a mixture of $TiCl_4$/PhCl (1:1 vol., Ti/Mg = 10) in the presence of DBP (DBP/Mg = 0.2) at 110 °C for 1 h and followed by two treatments with the same $TiCl_4$/PhCl mixture at 110 °C for 1 and 0.5 h.

All the catalysts were washed once with PhCl and three times with heptane.

2.4. Treatment of the samples with $AlEt_3$

The DBP/$MgCl_2$ sample was treated with $AlEt_3$ in heptane at [$AlEt_3$] = 7.5 mmol/l and Al/DBP molar ratio of 7.5 at 50 °C for 0.5 h and followed by two washings with heptane.

The catalysts (I) and (II) were treated with $AlEt_3$ in heptane at [$AlEt_3$] = 7.5 mmol/l and Al/Ti molar ratio of 20 at 50 °C for 0.5 h in the absence of an external donor or in the presence of the external donor ($PrSi(OMe)_3$ at $AlEt_3$/Si = 10 for catalyst (II)) and followed by two washings with heptane.

2.5. Chemical analysis

Titanium and aluminum content in the samples was determined with inductively coupled plasma-atomic emission spectrometry (ICP-AES). The DBP content was determined by reverse phase high performance liquid chromatography. The content of alkoxysilanes was determined by gas chromatography after dissolution of the sample in CH_3OH.

2.6. DRIFT measurements

The DRIFT spectra of dried samples were recorded on a Shimadzu FTIR-8400 spectrometer equipped with a dry nitrogen chamber and sealed cells with CaF_2 windows. All spectra were recorded with a nominal resolution of 4 cm^{-1}.

3. Results and discussion

At the interaction of titanium–magnesium catalysts with $AlEt_3$ cocatalyst, the set of processes proceeds: (1) the reduction of $TiCl_4$, (2) the removal of a part of internal donors, (3) the adsorption of external donors and aluminum compounds on the catalyst surface. The products of the interaction of $TiCl_4$ and $AlEt_3$, in particular $AlEt_2Cl$, can influence processes of the removal and adsorption of donors on the catalyst surface. The effect of $AlEt_3$ on the removal of the internal donor DBP from the $MgCl_2$ support surface in the absence of $TiCl_4$ was therefore specially checked. The use of the preliminary prepared $MgCl_2$ support, which was earlier used at
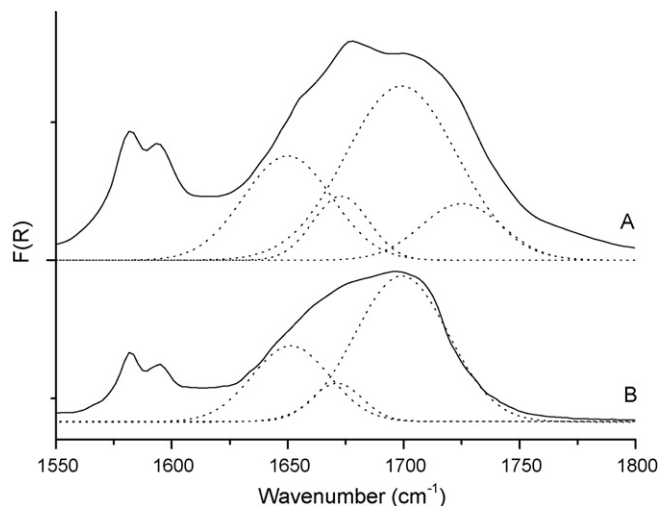

Fig. 1. DRIFT spectra of the DBP/$MgCl_2$ sample before (A) and after (B) interaction with $AlEt_3$ (samples 1 and 2 of Table 1), possible deconvolution is shown by dotted lines.

the studies of its interaction with the separate components of catalytic system (DBP, $TiCl_4$ and different organoaluminium compounds [12,31]), allows us to reveal the influence of these separate components of the catalytic system on the removal of DBP by the cocatalyst from the catalyst surface.

3.1. Interaction of DBP-containing support with $AlEt_3$

The used $MgCl_2$ support adsorbs DBP in the amount of 250 μmol/g $MgCl_2$ (Table 1, sample 1). At that, several complexes of DBP are formed on the support surface. These complexes can be characterized by IR-spectroscopy by position of absorption bands of carbonyl groups of DBP. Using the set of DBP/$MgCl_2$ samples differed by DBP content more than 100 times and $TiCl_4$/DBP/$MgCl_2$ catalyst, we have proposed the positions of $\nu(C=O)$ of carbonyl groups of DBP in its individual complexes on the surface of highly dispersed $MgCl_2$: 1650, 1672 and 1699 cm^{-1} [12]. All the experimental spectra of carbonyl groups were well described by the number of Gaussian functions with the mentioned set of $\nu(C=O)$ frequencies.

Fig. 1A shows DRIFT spectrum of the DBP/$MgCl_2$ sample (Table 1, sample 1) in the range of $\nu(C=O)$ bands. This spectrum is a superposition of four separate bands. The bands at 1650, 1672 and 1699 cm^{-1} presumably correspond to DBP complexes with surface-exposed Mg ions in different chlorine coordination: 3, 4 or 5 chlorine atoms (Q^3, Q^4 or Q^5 complexes, correspondingly) [12,30]. It is possible also, that DBP can form complexes of different stoichiometries with respect to surface-exposed Mg ions of equal chlorine coordination. The high frequency band at 1722 cm^{-1} belongs to loosely coordinated DBP, in which one or two carbonyl groups are hydrogen-bonded only. The amount of different DBP complexes is shown in Table 1 (sample 1). About half of DBP on the support surface presents as more weak Q^5 complexes with $\nu(C=O)$ of carbonyl groups close to 1699 cm^{-1}.

At the interaction of sample 1 with $AlEt_3$, the amount of DBP on the $MgCl_2$ surface decreases almost two times (Table 1, sample 2). $AlEt_3$ adsorbs on the support surface so as the total amount of DBP and adsorbed $AlEt_3$ is equal to the initial amount of DBP in sample 1 before the interaction with $AlEt_3$. Seemingly, $AlEt_3$ adsorbs on surface sites released by the removal of DBP. DRIFT spectrum of sample 1 after the interaction with $AlEt_3$ is shown in Fig. 1B. The data on the amount of DBP complexes obtained by deconvolution of the spectrum are presented in Table 1 (sample 2). These data

Table 1
The effect of the AlEt$_3$ interaction with the DBP-containing support and catalysts on chemical composition and the content of different DBP complexes.

No	Sample	Chemical composition, μmol/g MgCl$_2$				Content of DBP complexes (μmol/g MgCl$_2$) differed by carbonyl groups at (cm^{-1})[a]				
		DBP	Ti	Al	Total[b]	1650 Q^3	1672 Q^4	1699 Q^5	1722–1734[c]	1752–1755[d]
1	DBP/MgCl$_2$	250	0	0	250	65	25	130	30	0
2	DBP/MgCl$_2$–AlEt$_3$	140	0	110	250	38	12	90	0	0
3	Cat. (I): TiCl$_4$/DBP/MgCl$_2$	120[e]	180	0	300	23	12	55	0	30
4	Cat. (I)—AlEt$_3$	75[e]	135	180	390	35	0	32	0	8
5	Cat. (II): TiCl$_4$/DBP/MgCl$_2$	485[e]	495	0	980	130	20	255	20	60
6	Cat. (II)—AlEt$_3$	250	365	700	1315	110	15	125	0	0
7	Cat. (II)—AlEt$_3$/PTMS	260[e]	340	590	1395[f]	95	20	125	0	20

[a] Determined via deconvolution of DRIFT spectra.
[b] Total amount of surface compounds.
[c] Free or loosely coordinated DBP.
[d] Phthaloyl chlorides.
[e] Including phthaloyl chlorides.
[f] Including PrSi(OMe)$_3$ (45 μmol/g MgCl$_2$) and Et(Pr)Si(OMe)$_2$ (160 μmol/g MgCl$_2$).

show that at the interaction of the DBP/MgCl$_2$ sample with AlEt$_3$ the partial removal of all the types of the surface DBP complexes occurs without marked preference to any type of these complexes. So, the interaction of AlEt$_3$ with DBP is not selective towards any type of DBP complexes. Loosely coordinated DBP characterizing by ν(C=O) of carbonyl groups at 1722 cm^{-1} is removed completely.

3.2. Interaction of catalyst (I) with AlEt$_3$

At synthesis of a catalyst, TiCl$_4$ and DBP compete with each other for adsorption sites of the MgCl$_2$ surface. In our case, the surface area of catalyst (I) (about 100 m^2/g) is close to that of the initial MgCl$_2$ support. The sum of DBP and TiCl$_4$, adsorbed on the catalyst surface, is close to the amount of DBP adsorbed on the initial MgCl$_2$ support. Therefore, we conclude that the amount and distribution of adsorption sites on the support surface remains practically unchanged during the catalyst preparation, and the main part of TiCl$_4$ adsorbs in catalyst (I) on the sites, which are occupied by the part of surface DBP complexes in the DBP/MgCl$_2$ sample [12]. Only small part of TiCl$_4$ adsorbs on surface sites, which are not available for adsorption of DBP, seemingly, because of steric reasons. So, the main part of TiCl$_4$ and DBP, at the least, does not interact with each other in the catalyst. The same has been earlier shown in [8]: the internal donor interacts only with MgCl$_2$ in catalysts of well performance, and complexes of donor with TiCl$_4$ formed at beginning of catalyst synthesis being removed at following stages of synthesis. However, there is an opposite point of view too [5,29], that a part of TiCl$_4$ forms complexes with the internal donor in catalysts, with carbonyl bands of the internal donor appearing in IR spectra close to 1650 cm^{-1} [29].

Note here, the absence of complexes of TiCl$_4$ with an internal donor in catalysts can be excluded by data of IR-spectroscopy in the following way. The ν(C=O) bands of carbonyl groups of esters present in catalyst are in the range of 1650–1700 cm^{-1} (Fig. 2A). Nearly to these bands, the bands of phenyl ring are in the low-frequency region (1580–1600 cm^{-1}). The bands of phenyl ring appear as the doublet because of ortho-substituted phenyl ring in the case of aromatic diesters or because of conjunction of π-system of phenyl ring with carbonyl group in the case of aromatic monoester [32]. Intensities of bands of the doublet are close with each other (look for example Fig. 2A and majority of literature data including [29]). If TiCl$_4$·DBP complexes are formed, the ν(C=O) band of DBP splits in two bands [6,8] because of Fermi resonance with combinational bands of phenyl ring [32]. At that, one band appears in the range of 1640–1650 cm^{-1}, another one appearing in the range of bands of phenyl ring at ca. 1585 cm^{-1}. Because of that, the doublet of the bands of phenyl ring disappears (visually two

bands join) or relative intensities of bands of the doublet change markedly as compared with ones of esters adsorbed on MgCl$_2$ only. A change of relative intensities of bands of phenyl ring or its merging in one band is the fact testifying to a formation of noticeable amount of TiCl$_4$·ester complexes. In our case close intensities of bands of phenyl ring in the range of 1580–1600 cm^{-1} (Fig. 2A) point to the absence of noticeable amounts of TiCl$_4$·DBP complexes. The recent study [16] also proved the absence of TiCl$_4$·DBP complexes in titanium–magnesium catalysts.

Since DBP and TiCl$_4$ are present on the catalyst surface independently with each other, then the removal of DBP from the catalysts surface by AlEt$_3$ has seemingly to possess the same regularity as at the removal of DBP from the DBP/MgCl$_2$ sample. The content of DBP and titanium in catalyst (I) decreases at the interaction of catalyst (I) with AlEt$_3$ (Table 1, sample 4). Simultaneously, aluminum compounds adsorb on the catalyst surface, and the amount of these compounds markedly exceeding the amount of removed DBP and titanium. The marked changes occur in DRIFT spectrum of carbonyl groups (Fig. 2B). The main part of phthaloyl chlorides (ν(C=O) = 1752 cm^{-1}) is removed, with the maximum of the carbonyl bands of phthaloyl chlorides shifting to 1744 cm^{-1}. The displacement of this maximum indicates that phthaloyl chlorides also form several surface complexes as DBP. The content and the fraction of more strong DBP complexes (ν(C=O) = 1650 cm^{-1}) increase compared with the initial catalyst (I). Seemingly, a part
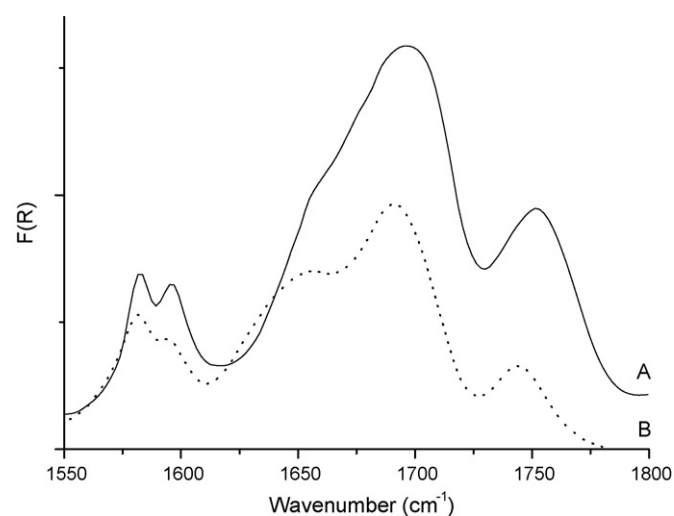

Fig. 2. DRIFT spectra of catalyst (I) before (A) and after (B) interaction with AlEt$_3$ (samples 3 and 4 of Table 1).
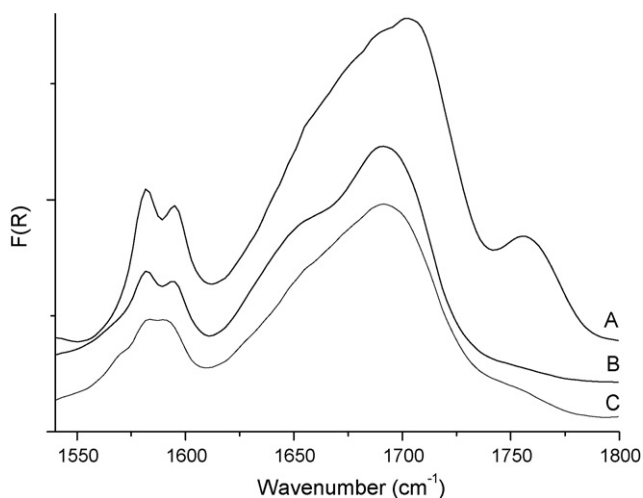
Fig. 3. DRIFT spectra of catalyst (II) before (A) and after interaction with AlEt$_3$ (B) or with AlEt$_3$/PTMS mixture (C) (samples 5, 6, 7 of Table 1, respectively).

of removed DBP can form new strong complexes on new adsorption sites of the catalyst surface. These new adsorption sites can be AlEt$_2$Cl, which forms at the interaction of AlEt$_3$ with TiCl$_4$ and adsorbs on the surface of titanium–magnesium catalysts [27,33]. A large part of adsorbed AlEt$_2$Cl contains coordinatively unsaturated alumina (30–40% of alumina content) and is able to adsorb electron-donor compounds [27,33]. As it was shown for ethyl benzoate [34], ν(C=O) bands of ester complexes with AlEt$_2$Cl are at ~1650 cm^{-1}. The distinctive feature of the formation of these complexes is a marked increase of intensity of the phenyl ring band at ~1580 cm^{-1} in contract to the band at ~1600 cm^{-1} [34]. In our case, as Fig. 2B shows, a marked increase of the band intensity at ~1582 cm^{-1} occurs relative to the band at ~1595 cm^{-1} in comparison with the two ones in the spectrum of the initial catalyst (Fig. 2A). Seemingly, such spectral changes indicate, by analogy with EB [30], a formation of DBP complexes with AlEt$_2$Cl. In addition, some new adsorption sites can arise from coordinatively unsaturated titanium species (TiCl$_3$), which form during the reduction of TiCl$_4$ by AlEt$_3$. Complexes of esters with TiCl$_3$ seem to contribute to IR spectra, in the region under discussion, similarly to complexes of esters with AlEt$_2$Cl [28]. Nevertheless, the amount of coordinatively unsaturated titanium species should not exceed the amount of active sites, usually several percents of titanium content only. Therefore, complexes of DBP with AlEt$_2$Cl are most probably responsible for the spectral changes.

The presence of DBP complexes with new adsorption sites impedes the study of the removal of initial DBP complexes from the catalyst surface. At the same time, the presence of these DBP complexes indicates that not all DBP, analytically determined in a catalyst treated by AlEt$_3$, can belong to DBP complexes present in initial catalyst.

3.3. Interaction of catalyst (II) with AlEt$_3$

Catalyst (II) contains considerably larger amounts of TiCl$_4$ and DBP than catalyst (I) (Table 1, samples 3 and 5). This is the result of much higher surface area of catalyst (II) (about 280 m^2/g) in comparison with the surface area of catalyst (I) (about 100 m^2/g). DRIFT spectrum of catalyst (II) is shown in Fig. 3A, and the distribution of different DBP complexes being presented in Table 1 (sample 5). A set of differences is observed against catalyst (I). The lesser portion of –C=O-groups falls on phthaloyl chlorides, seemingly because of somewhat low temperature during the catalyst preparation (110 °C instead of 115 °C for catalyst (I)). The portion

of more strong DBP complexes (Q^3) is slightly higher in catalyst (II). The last most likely is the result of different methods of formation of catalyst (II), that leads to more developed surface of catalyst (II) and, seemingly, to a larger portion of surface magnesium ions, possessing by larger coordination unsaturation. Nevertheless, Q^5 complexes are the main DBP complexes for both catalysts.

During the interaction of catalyst (II) with AlEt$_3$ the changes of its chemical composition are similar with the ones for catalyst (I) (Table 1, samples 4 and 6). The content of DBP and titanium decreases essentially. Alumina compounds enter in sample 6 in much higher amounts compared with sample 4. DRIFT spectrum of catalyst (II) changes markedly (Fig. 3B). ν(C=O) bands of –COCl groups (at ~1755 cm^{-1}) disappear completely, and the shoulder at 1650 cm^{-1} arisen from Q^3 complexes becoming more pronounced. The complete removal of phthaloyl chlorides at the interaction of a catalyst with AlEt$_3$ was found also in [29]. As the data of the spectrum deconvolution show, the amount of more weak Q^5 complexes becomes close to the amount of more strong Q^3 complexes. Note, there is no qualitative changes of the spectrum in the range of bands of phenyl ring upon the treatment of catalyst (II) by AlEt$_3$. This allows us to conclude that DBP is mainly bound with MgCl$_2$ in sample 6 and does not form marked quantities of complexes with AlEt$_2$Cl. On the whole, complexes of phthaloyl chlorides and Q^5 complexes of DBP are firstly removed at the interaction of catalyst (II) with AlEt$_3$ just as for the model catalyst (I). As compared with the DBP/MgCl$_2$ sample without TiCl$_4$, the preferred removal of Q^5 complexes occurs in catalysts (I) and (II). This difference seems to occur because of the presence of high amount of alumina compounds in samples 4 and 6, AlEt$_2$Cl as a product of interaction of AlEt$_3$ and TiCl$_4$, in comparison with sample 2. Possibly, AlEt$_2$Cl promote the removal of more weak Q^5 complexes in addition to the main effect of AlEt$_3$.

The titanium and DBP content in the catalyst (II) treated by the mixture of AlEt$_3$ with propyltrimethoxysilane, PTMS (Table 1, sample 7) does not practically differ from that of catalyst (II) treated by alone AlEt$_3$ (sample 6). At the same time, the alumina content decreases markedly and silane compounds (PTMS and Et(Pr)Si(OMe)$_2$, as the product of the reaction of PTMS and AlEt$_3$) adsorb on the catalyst surface. The distribution of DBP complexes of sample 7 does not practically differ from that of sample 6, excluding a slight decrease of the amount of more strong Q^3 complexes and the presence of some amount of –COCl groups (Fig. 3C). On the whole, PTMS does not promote any selective removal of DBP complexes at the interaction of the catalyst with AlEt$_3$. At the same time, the retention of the total amount and the distribution of DBP surface complexes accompanied by the decrease of the alumina content can indicate that a part of silane compounds adsorbs on the MgCl$_2$ surface sites released by the removal of DBP and TiCl$_4$.

4. Conclusions

The performed study showed that AlEt$_3$ partially removes all types of DBP complexes from the MgCl$_2$ support surface, and AlEt$_3$ being adsorbed on the MgCl$_2$ surface in place of removed DBP. Contrary to the MgCl$_2$ support, during the interaction of the catalysts with AlEt$_3$, the removal of DBP complexes occurs, to a greater extent, owing to the removal of more weak DBP complexes. It is possible, chloroorganic alumina compounds, formed during interaction of catalysts with AlEt$_3$, influence the removal of these more weak DBP complexes. A part of removed DBP can adsorb again on the catalyst surface as complexes with chloroorganic alumina compounds. Loosely coordinated DBP and complexes of phthaloyl chlorides are almost completely removed by AlEt$_3$. The external donor alkylalkoxysilane does not markedly influence the removal of different DBP complexes.

If we compare the obtained data for DBP with the data obtained for monoester ethylbenzoate [30], two aspects can be noticed. (1) The preferable removal of more weak Q^5 complexes from the $MgCl_2$ support was observed in the case of EB in contrast to nonselective removal of all the types of DBP complexes. It seems to be the result of bidentate coordination of DBP in contrast to monodentate coordination of EB, as the different strengths of different DBP complexes are not determinative factor at the removal of DBP complexes by $AlEt_3$, contrary to the removal of EB complexes. The effect observed at the removal of different EB and DBP complexes from the $MgCl_2$ support surface by $AlEt_3$ is similar with that of $TiCl_4$ at preparation of catalysts. $TiCl_4$ also removes more weak Q^5 complexes of EB mainly and nonselectively removes different DBP complexes [12]. (2) For both internal donors, a part of internal donor removed during interaction with $AlEt_3$ can adsorb again on the catalysts surface in the form of complexes with chloroorganic alumina compounds.

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