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DRIFTS study of the interaction of the AlEt$_3$ cocatalyst with the internal donor ethyl benzoate in supported Ziegler–Natta catalysts

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ABSTRACT

The interaction of AlEt$_3$ cocatalyst with the internal donor (ethyl benzoate–EB) in the supported Ziegler–Natta (TiCl$_4$/EB/MgCl$_2$) catalysts and the EB/MgCl$_2$ support was studied by DRIFT spectroscopy. For EB/MgCl$_2$ samples, it was shown that AlEt$_3$ firstly removed the more weak surface complexes of EB from the MgCl$_2$ surface and competed with EB at adsorbtion for releasing sites of the MgCl$_2$ surface. EB, as the external donor, keeps constant the initial content and distribution of surface complexes of EB at the interaction of the AlEt$_3$/EB mixture with the EB/MgCl$_2$ support. At the interaction of AlEt$_3$ with the TiCl$_4$/EB/MgCl$_2$ catalysts one type of surface complexes of EB is mainly removed. A part of removed EB adsorbs again on the catalyst surface in the form of complexes with aluminum-containing compounds. At the interaction of the catalyst with the AlEt$_3$/EB mixture the EB content in the catalyst changes slightly, but the distribution of different surface complexes of EB in the catalyst changes noticeably compared to that in the initial catalyst. EB, as the external donor, adsorbs both on surface MgCl$_2$ sites released at the removal of the internal donor and on aluminum-containing compounds adsorbed on the catalyst surface.

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1. Introduction

The introduction of the Lewis bases ("internal donors") into supported Ziegler–Natta catalysts greatly influences the performance of these catalysts in propene polymerization, especially the stereospecificity of the catalysts [1]. The internal donor (ID) in catalysts of the TiCl$_4$/ID/MgCl$_2$ composition provides high stereospecificity above 95% at short polymerization time [2,3]. However, with the increase of polymerization time a part of the internal donor is removed from the catalysts as the result of the interaction of the catalysts with cocatalyst (aluminum trialkyl) [2–8]. The removal of a part of the internal donor from the catalysts is accompanied by drastic decrease of stereospecificity of the catalysts. A decrease of stereospecificity of the catalysts results in a decrease of yield of iso-tactic polymer and in an increase of portion of atactic polymer [2]. A part of the internal donor remains in the catalysts and, possibly, owing to that the stereospecificity of the catalysts exceed the stereospecificity of the catalyst with the composition of TiCl$_4$/MgCl$_2$, which does not contain the internal donor initially [3]. To keep high stereospecificity of the catalysts, external donors are intro-duced in polymerization medium. The external donors adsorb on the surface of the catalysts, for example [1,9], and thereby keep high stereospecificity of the catalysts.

We have earlier shown that surface complexes formed at the interaction of carbonyl groups of the internal donors with highly dispersed support MgCl$_2$ in samples ID/MgCl$_2$ and TiCl$_4$/ID/MgCl$_2$ catalysts (where ID = ethyl benzoate or di-n-butyl phthalate) can be characterized by IR spectroscopy of diffuse reflection (DRIFTS) by position of absorbtion bands of carbonyl groups in IR spectra [10]. It was found that the internal donors form several types of complexes with low-coordinated Mg ions on the support surface. A part of these complexes was removed by TiCl$_4$ at preparation of the catalysts, with TiCl$_4$ having adsorbed on the support surface instead of removed donors. The use of DRIFT spectroscopy allowed us to determine what surface sites were occupied by main part of adsorbed TiCl$_4$ [10].

In the present work we used DRIFTS to study the interaction of the support EB/MgCl$_2$ and the TiCl$_4$/EB/MgCl$_2$ catalysts with AlEt$_3$ cocatalyst. Two types of the catalysts were investigated: (i) the catalyst prepared by the interaction of TiCl$_4$ and EB with highly dispersed MgCl$_2$; (ii) the catalyst prepared by the interaction of TiCl$_4$ and EB with Mg(OEt)$_2$. In the last the formation of the support (MgCl$_2$) takes place during the catalyst preparation via chlorina-tion of Mg(OEt)$_2$ by TiCl$_4$. The first catalyst is, to a greater extent, a model catalyst. While the second one, by the way of preparation, corresponds to modern supported catalysts. The use of these two

catalysts allows us to extend the data for model samples to real catalysts.

2. Experimental

2.1. Materials

Heptane, n-butylchloride, chlorobenzene (PhCl), EB were used after dehydration over molecular sieves. All the preparation and manipulation with samples were performed under argon atmosphere. Argon gas was additionally 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 interaction of magnesium metal powder with C_4H_9Cl (molar ratio $C_4H_9Cl/Mg = 3$) in heptane at 98 °C with subsequent washing with heptane. The resulting $MgCl_2$ support contained ca. 5 wt.% of organic residue and had a surface area of ca. 100 m^2/g.

2.3. Preparation of samples

The $EB/MgCl_2$ sample (3.6 wt.% or 250 μmol of EB per gram of $MgCl_2$) was prepared by adding EB to a suspension of $MgCl_2$ ($EB/MgCl_2 = 0.1$) in PhCl (25 ml/g of $MgCl_2$) at 105 °C and keeping the reaction mixture at this temperature for 1 h. The resulted sample was washed once with PhCl at 105 °C and twice with heptane.

Titanium–magnesium catalyst (**I**) with a composition of $TiCl_4/EB/MgCl_2$ (0.77 wt.% of Ti (170 μmol/g $MgCl_2$), 1.5 wt.% of EB (105 μmol/g $MgCl_2$)) 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 EB (EB/Mg = 0.1) at 105 °C for 1 h and followed by two treatments with the same $TiCl_4$/PhCl mixture at 105 °C for 0.5 h.

Titanium–magnesium catalyst (**II**) with a composition of $TiCl_4/EB/MgCl_2$ (2.4 wt.% of Ti (615 μmol/g $MgCl_2$), 9.2 wt.% of EB (755 μmol/g $MgCl_2$)) 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 EB (EB/Mg = 0.3) at 105 °C for 1 h and followed by one treatment with the same $TiCl_4$/PhCl mixture in the presence of EB (EB/Mg = 0.2) at 105 °C for 0.5 h and one treatment with the same $TiCl_4$/PhCl mixture at 105 °C for 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 $EB/MgCl_2$ sample was treated with $AlEt_3$ in heptane at $[AlEt_3] = 7.5$ mmol/l and Al/EB molar ratio of 7.5 for 0.5 h at 50 °C and followed by two washings with heptane.

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

The catalyst (II) was treated with $AlEt_3$ in heptane at $[AlEt_3] = 7.5$ mmol/l and Al/Ti molar ratio of 20 for 0.5 h at 50 °C in the presence or absence of the external donor (EB at $AlEt_3$/EB = 3) and followed by two washings with heptane.

2.5. Chemical analysis

Titanium and aluminum content in the samples was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The content of EB was determined by reverse phase High Performance Liquid Chromatography.

2.6. DRIFT spectroscopy

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

Using the set of the $EB/MgCl_2$ samples differed by EB content in a number of cases more than 50 times and for $TiCl_4/EB/MgCl_2$ catalyst we have earlier proposed the positions of ν(C=O) of carbonyl groups of EB in its individual complexes on the surface of highly dispersed $MgCl_2$: 1645, 1675 and 1695 cm^{-1} [10]. All the experimental spectra of carbonyl groups were well described by the number of Gaussian functions with the mentioned set of ν(C=O) frequencies. Quite recently it was asserted in [11] that bands of ν(C=O) of esters observed in IR spectra of titanium–magnesium catalyst with bands position close to 1650 cm^{-1} have been arisen from complexes of esters and $TiCl_4$ only. Simultaneously, if these bands are present in IR spectra of ester/$MgCl_2$ samples, they are the result of contamination of these samples by water [11]. This assertion forced us to make short preface and additional contribution to our present work. To avoid ambiguity at the interpretation of the data of our present work, we firstly discuss the origin of low-frequency bands observed in IR spectra in the range of ν(C=O) bands.

Fig. 1 shows the examples of DRIFT spectra of highly dispersed $MgCl_2$. Sometimes traces of water can be present in the sample. The water has the following appearance in the spectra (Fig. 1A): the band at 1613 cm^{-1} arising from δ(HOH) of adsorbed H_2O, corresponding overtones at 3200 cm^{-1}, ν(OH) of H_2O and hydroxyls in the range of 3200–3700 cm^{-1}. The band of δ(HOH) at 1613 cm^{-1} is well described by Gaussian function. Fig. 1A and B shows the changes of DRIFT spectrum at washing of the $MgCl_2$ with heptane from which not all water had been removed by drying. At this case the drastic increase of δ(HOH) is observed (Fig. 1B). The band position shifts slightly from 1613 to 1618 cm^{-1}. The shape of the band does not change. The intensities of ν(OH) in the range of 3200–3700 cm^{-1} increase proportionally to the increase of the intensity of δ(HOH). So, the presence of H_2O does not produce addi-
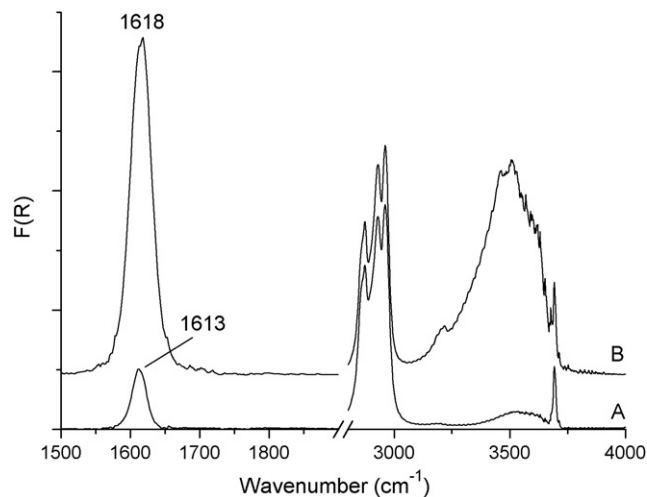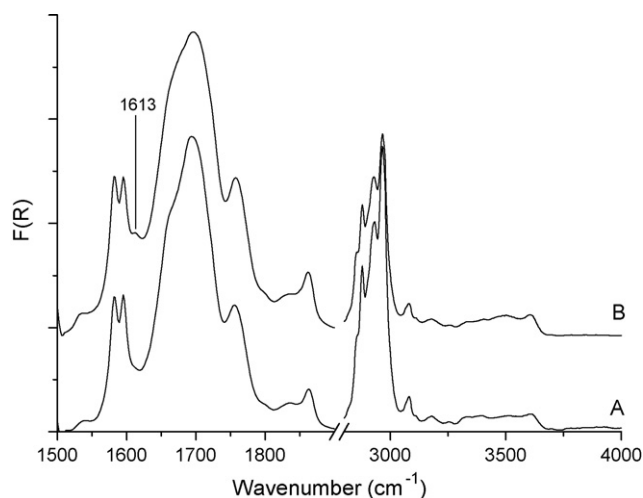

Fig. 1. DRIFT spectra of the highly dispersed $MgCl_2$ demonstrating the influence of water on the spectra: before (A) and after (B) additional washing by undehydrated heptane.
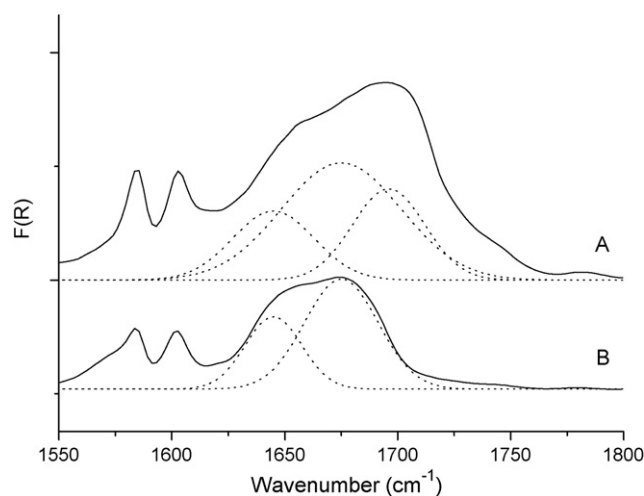
Fig. 2. DRIFT spectra of catalysts containing esters as internal donors: a spectrum without marked demonstration of H_2O (A) and a spectrum with weak $\delta(HOH)$ at 1613 cm^{-1} (B).

Fig. 3. DRIFT spectra of the EB/MgCl$_2$ sample before (A) and after (B) interaction with AlEt$_3$ (samples 1 and 2 of Table 1), possible deconvolutions of spectra are shown by dotted lines.

tional bands around 1650 cm^{-1}, which were orally mentioned in [11]. Fig. 2 shows the example of appearance of $\delta(HOH)$ band in the spectra of titanium–magnesium catalysts containing esters as the internal donors. It is seen that a weak band of $\delta(HOH)$ at 1613 cm^{-1} is present near to the duplet of phenyl ring (Fig. 2B) as compared with a catalyst without marked demonstration of H_2O (Fig. 2A). On the whole, the same influence of H_2O on IR spectra of supported titanium–magnesium catalysts was shown a long time ago [12]. So, the bands at ca. 1650 cm^{-1} present in IR spectra of esters adsorbed on the surface of MgCl$_2$ belong unambiguously to $\nu(C=O)$ bands of esters in complexes of esters and MgCl$_2$.

3.1. Interaction of the EB-containing support with AlEt$_3$

It was firstly studied the interaction of AlEt$_3$ with the EB/MgCl$_2$ sample obtained by the treatment of highly dispersed MgCl$_2$ with EB in chlorobenzene medium. The state of EB in such a sample has been earlier studied by DRIFT spectroscopy [10]. Fig. 3A shows the DRIFT spectrum of the EB/MgCl$_2$ sample (Table 1, sample 1) in the range of the $\nu(C=O)$. It has been earlier shown via computer-assisted deconvolution of the DRIFT spectrum of such sample that EB forms several types of surface complexes [10]. These complexes (Table 1, sample 1) correspond to complexes of EB with surface-exposed Mg ions in different chlorine coordination, for example, with 3, 4 or 5 chlorine atoms at Mg ion (complexes Q^3, Q^4 and Q^5, correspondingly). It is believed that more strong complexes Q^3 and

Q^4 correspond to $\nu(C=O)$ in the range of low frequencies (1645 and 1675 cm^{-1}) [10]. It is possible also that EB is able to form at one of the MgCl$_2$ faces complexes of different stehiometry with respect to surface-exposed Mg ions. About half the complexes of EB (46%) are in the form of Q^4 complexes and 20% of EB are in the form of more weak (Q^5) and more strong (Q^3) complexes (sample 1, Table 1).

At the interaction of the EB/MgCl$_2$ sample with AlEt$_3$ the half of EB (130 μmol/g) is removed and surface complexes of AlEt$_3$ (120 μmol/g) are formed (Table 1, sample 2). As Table 1 shows, the total amount of surface EB and Al compounds does not practically change. Note, that in the absence of EB the interaction of AlEt$_3$ with similar MgCl$_2$ support resulted in formation of surface complexes of AlEt$_3$ in close to EB quantities (250 μmol/g) [13]. So, at the interaction with EB/MgCl$_2$ sample AlEt$_3$ occupies coordination sites at MgCl$_2$ surface available after removal of a part of EB. As the data of Table 1 (samples 1 and 2) and Fig. 3 show, these sites mainly appear owing to the removal of Q^5 complexes and loosely coordinated EB characterized by $\nu(C=O)$ above 1700 cm^{-1}. As the result, sample 2 contains EB in the form of Q^3 and Q^4 complexes only (sample 2, Fig. 3B).

Sample 3 obtained at the interaction of sample 1 with AlEt$_3$/EB mixture (EB as the external donor at AlEt$_3$/EB = 3) contains the same quantity of EB practically as sample 1. Adsorbtion of AlEt$_3$ is small in this case. DRIFT spectra of samples 3 and 1 are very similar (Fig. 4), and, as the data of Table 1 show (sample 3), the distribution of different EB complexes does not change practically compared to sample

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

No.	Sample	Chemical composition, μmol/g MgCl$_2$				Content of EB complexes (μmol/g MgCl$_2$) differed by carbonyl groups at (cm^{-1})[a]			
		EB	Ti	Al	Total	1645 Q$_3$	1675 Q$_4$	1695 Q$_5$	>1700[b]
1	EB/MgCl$_2$	250	0	0	250	50	115	55	30
2	EB/MgCl$_2$ + AlEt$_3$	120	0	120	240	40	80	0	0
3	EB/MgCl$_2$ + (AlEt$_3$/0.3EB)	260	0	40	300	60	125	60	15
4	MgCl$_2$ + (AlEt$_3$/0.3EB)	150	0	75	225	55	60	30	5
5	Cat. (I): TiCl$_4$/EB/MgCl$_2$	105	170	0	275	25	75	5	0
6	Cat. (I) + AlEt$_3$	32	145	180	357	19	13	0	0
7	Cat. (II): TiCl$_4$/EB/MgCl$_2$	755	615	0	1370	70	545	30	110
8	Cat. (II) + AlEt$_3$	405	520	360	1285	140	190	20	55
9	Cat. (II) + (AlEt$_3$/0.3EB)	680	480	210	1370	160	320	90	110

[a] Determined via deconvolution of DRIFT spectra.
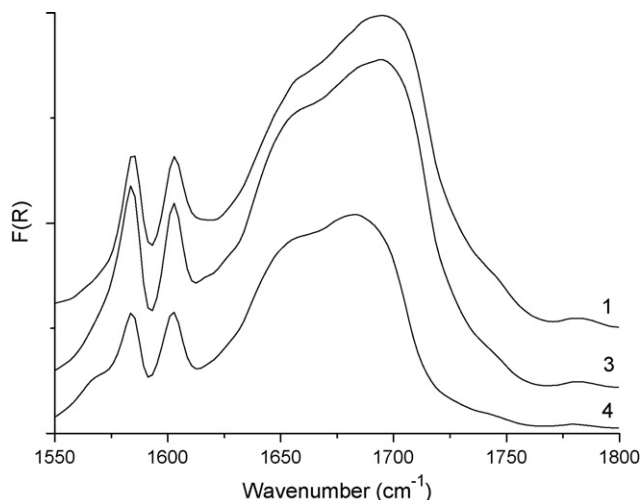[b] Free or weakly bound carbonyl groups.

Fig. 4. DRIFT spectra of samples 1, 3 and 4 from Table 1.

Fig. 5. DRIFT spectra of catalyst (I) before (solid line) and after (dotted line) interaction with AlEt$_3$ (samples 5 and 6 of Table 1).

1. So, it is possible to believe, if the removal of EB from the MgCl$_2$ surface takes place, then EB from the solution occupies its places and keeps the initial distribution of EB complexes on the MgCl$_2$ surface.

Data obtained after the interaction of MgCl$_2$ support with the mixture of AlEt$_3$ and EB (AlEt$_3$/EB = 3) (sample 4) show that the formation of MgCl$_2$ complexes with EB is more preferable than with AlEt$_3$, in spite of threefold excess of AlEt$_3$ with respect to EB. As Fig. 4 and the data of Table 1 (sample 4) show, the portion of more strong complexes Q^3 increases in sample 4 compared to samples 1–3.

Thus, the data obtained show that AlEt$_3$ can remove considerable part of more weak complexes of EB from the MgCl$_2$ surface and does not remove EB, from formal point of view, with the use of AlEt$_3$/EB mixture (AlEt$_3$/EB = 3).

3.2. Interaction of catalysts with AlEt$_3$

The data on the EB and Ti content and the distribution of different complexes of EB in catalyst (I) are shown in Table 1 (sample 5). DRIFT spectrum of this catalyst is presented in Fig. 5. In spite of great excess of TiCl$_4$ at the catalyst preparation (TiCl$_4$/EB = 100), considerable amounts of EB complexes (105 μmol/g) form on the MgCl$_2$ surface besides the adsorbtion of TiCl$_4$. These complexes are formed as the complexes Q^3 and Q^4 with more acidic sites of the MgCl$_2$ surface. The rest adsorbtion sites of MgCl$_2$ are obviously occupied by TiCl$_4$. The sum of EB and TiCl$_4$ in catalyst (I) (275 μmol/g) is close to the content of adsorbtion sites of the initial MgCl$_2$ support with respect to EB adsorbtion (250 μmol/g, sample 1).

When interacting with AlEt$_3$ (sample 6), the content of EB in catalyst (I) decreases (by three times). The content of titanium decreases to a lesser extent (by 15% only). At the same time, considerable amounts of aluminum-containing compounds adsorb on the catalyst surface. The total number of surface species (EB, titanium and aluminum compounds) markedly exceeds the sum of EB and TiCl$_4$ in the initial catalyst (I). This can indicate on the formation of additional sites in catalyst (I) available for adsorbtion of aluminum compounds, for example, surface compounds of titanium. Probably, aluminum compounds adsorb both MgCl$_2$ and titanium chlorides. The interaction of the catalyst (I) with AlEt$_3$ changes the spectrum of ν(C=O) of EB (Fig. 5). The main part of EB is in the form of complexes Q^3 in sample 6, unlike the initial sample 5. Qualitative changes of the spectrum in the region of absorbtion bands of phenyl ring are observed too (Fig. 5); the new band appears at ca. 1573 cm^{-1}. We suppose that the appearance of this band points to the formation
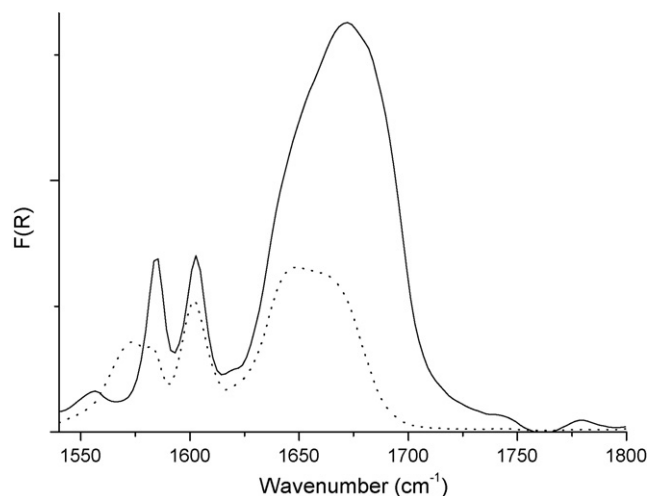
of EB complexes with AlEt$_2$Cl. Indeed, AlEt$_2$Cl, as a product of AlEt$_3$ interaction with TiCl$_4$, is the main surface compound of alumina in the catalysts [15], and a part of AlEt$_2$Cl present on the catalyst surface can adsorb electron-donor compounds [13]. According to the literature data [14], a low-frequency band at ca. 1580 cm^{-1} appears at the formation of EB complexes with AlEt$_2$Cl. At that, the ν(C=O) band of EB appears at ca. 1644 cm^{-1}. This is close to the ν(C=O) frequency (ca. 1645 cm^{-1}) of EB in Q^3 complexes on MgCl$_2$ surface. So, a part of Q^3 complexes contains EB complexes with AlEt$_2$Cl. Apparently, a part of EB removed from the MgCl$_2$ surface of catalyst (I) can adsorb again on new more acidic sites of the catalyst and produce the EB complexes with ν(C=O) corresponding to Q^3 complexes.

The data on the interaction of AlEt$_3$ with catalyst (II) are presented in Table 1 (samples 7–9) and Figs. 6 and 7. The amount of EB and TiCl$_4$ is significantly higher in catalyst (II) than in catalyst (I) (Table 1, samples 7 and 5). This is a result of that the surface area of catalyst (II) prepared from Mg(OEt)$_2$ is essentially higher (about 300 m^2/g) than the surface area of catalyst (I) prepared with the use of the MgCl$_2$ support of relatively low surface area (about 100 m^2/g). Besides, the ratio EB/TiCl$_4$ is markedly higher in catalyst (II) than that in catalyst (I) (1.2 instead of 0.6, correspondingly). The differences of the chemical composition and surface area of
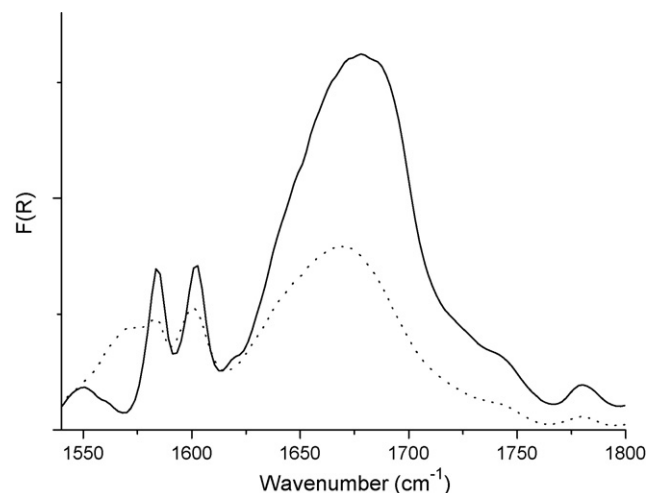

Fig. 6. DRIFT spectra of catalyst (II) before (solid line) and after interaction with AlEt$_3$ (dotted line) (samples 7 and 8 of Table 1).
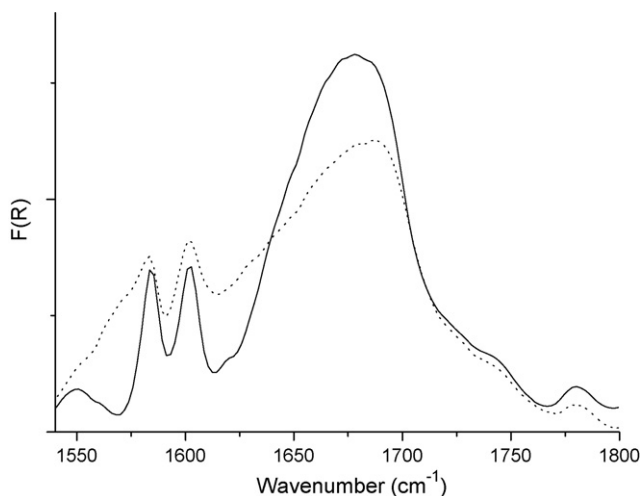
Fig. 7. DRIFT spectra of catalyst (II) before (solid line) and after interaction with AlEt$_3$/EB (dotted line) (samples 7 and 9 of Table 1).

catalysts (I) and (II) does not influence the distribution of surface complexes of EB practically. The main part of surface complexes of EB is in the form of complexes Q^4 (72%) in catalyst (II) as in catalyst (I). It means that EB in the presence of TiCl$_4$ interacts with one type of surface-exposed Mg ions mainly. At the same time, the set of different types of surface complexes of EB is similar for both the catalysts and the MgCl$_2$ support used in the study. That is, at formation of MgCl$_2$ during the preparation of catalyst (II), the same set of lateral faces of MgCl$_2$ is formed as for the MgCl$_2$ support. Indeed, as it was recently shown in [16], the presence of EB at the formation of MgCl$_2$ from Mg-containing support resulted in the formation of two basic types of lateral faces of MgCl$_2$ characterizing by different low-coordinated surface-exposed Mg ions. The formation of the (1 1 0) face with 4-coordinated Mg ions in the presence of EB indicates the directional interaction of EB with this face of MgCl$_2$. That submits completely to our data on predominant formation of one type of EB complexes (Q^4) in the catalysts.

At the interaction of catalyst (II) with AlEt$_3$, about half EB is removed; the titanium content decreases too, and surface complexes of aluminum compounds are formed (sample 8). The total number of surface species (EB, titanium and aluminum compounds) is equal to the sum of EB and TiCl$_4$ in the initial catalyst (II), in contrast to that in catalyst (I). As the data of DRIFT spectroscopy show (Fig. 6), the portion of more strong EB complexes (Q^3) increases markedly after the treatment of catalyst (II) by AlEt$_3$. The total amount of these complexes increases too as compared with the initial catalyst (Table 1, samples 7 and 8). The reason seems to be the formation of new EB complexes with new adsorbtion sites (AlEt$_2$Cl) on the catalyst surface. In favour of that, similarly to the case of sample 6, the fact of appearance in DRIFT spectrum of band at 1573 cm^{-1} indicates. This band, as before for sample 6, can be assigned to the complexes of EB with AlEt$_2$Cl formed in catalyst (II). Note, the amount of Q^3 complexes does not increase at the treatment of catalyst (I) by AlEt$_3$ (sample 6). We suppose that it is due to higher AlEt$_3$/EB ratio (2 times) at the treatment of catalyst (I) with AlEt$_3$ (as a result of constant AlEt$_3$/Ti ratio for both catalysts, but different EB/Ti ratios). So, in the case of catalyst (I), a removal of different EB complexes from the catalyst surface seems to proceeds to a greater extent than that with catalyst (II).

The interaction of catalyst (II) with AlEt$_3$ in the presence of EB as the external donor (AlEt$_3$/EB = 3) results in the minor decrease of the EB amount in the catalyst (sample 9 compared to sample 7). The EB amount is higher and the aluminum amount is lower in sample

9 than those in sample 8 prepared by the interaction of catalyst (II) with alone AlEt$_3$. The tendency of change of the EB and aluminum amount in samples 8 and 9 corresponds to that in samples 2 and 3 obtained by the interaction of sample 1 (EB/MgCl$_2$) with alone AlEt$_3$ or AlEt$_3$/EB mixture, correspondingly. The distribution of the EB complexes in sample 9 changes markedly compared to catalyst (II), that has not happened earlier at the interaction of sample 1 with the AlEt$_3$/EB mixture (sample 3). The changes happened with sample 9, as compared with the initial catalyst (II), indicate that chlorine-containing aluminum compounds formed at the interaction of catalyst (II) with AlEt$_3$ participate noticeably in the distribution of different complexes of EB. In the case of sample 9, the marked decrease of the amount of the Q^4 complexes and the increase of the amount of the Q^5 and Q^3 complexes are observed (Fig. 7, Table 1). The amount of more strong complexes of EB (Q^3) increases as in sample 8. At that a part of these complexes, as it was noted for sample 8, is probably in the form of EB complexes with chlorine-containing aluminum compounds. That is indicated by the presence of absorbtion band at 1573 cm^{-1} in DRIFT spectrum (Fig. 7).

4. Conclusion

For EB/MgCl$_2$ samples, it was shown that AlEt$_3$ cocatalyst firstly removed the more weak complexes of EB (Q^5 and weakly bound EB) from the MgCl$_2$ surface (ca. 50% of EB) and bound with the released surface sites of MgCl$_2$. The addition of EB as the external donor to AlEt$_3$ keeps constant the initial content and the distribution of surface complexes of EB at the interaction of the EB/MgCl$_2$ sample with the AlEt$_3$/EB mixture. The interaction of AlEt$_3$ with the TiCl$_4$/EB/MgCl$_2$ catalysts results mainly in the removal of the Q^4 complexes of EB, a part of the removed EB adsorbing again on catalyst surface, probably, in the form of complexes with aluminum compounds. At the interaction of the AlEt$_3$/EB mixture with the TiCl$_4$/EB/MgCl$_2$ catalyst the total amount of EB changes slightly, but the ratio between different types of surface EB complexes changes noticeably with increasing the portions of weak (Q^5) and more strong (Q^3) complexes of EB. EB as the external donor adsorbs both on the sites released at the removal of the internal donor and aluminum-containing compounds adsorbed on the catalyst surface. The model catalyst prepared with the use of highly dispersed MgCl$_2$ and the real catalyst prepared with the use of Mg(OEt)$_2$ show similar changes of their composition at the interaction with AlEt$_3$ cocatalyst. For both the catalysts, AlEt$_3$ cocatalyst mainly removes one type of surface complexes of EB, and a part of removed EB adsorbs again on the surface of the catalysts. So, the data obtained for the model catalyst and highly dispersed MgCl$_2$ support directly demonstrate the processes taking place on the surface of real supported catalysts at their interaction with cocatalyst and an external donor.

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