XPS study of the interaction of titanium species with internal electron donors on MgCl$_2$-supported Ziegler catalysts

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Abstract

Two types of MgCl$_2$-supported Ziegler catalysts prepared by a similar procedure with different internal electron donors were analyzed using X-ray photoelectron spectroscopy (XPS) to elucidate the interaction of the titanium species with the internal donors. The XPS measurement was also performed with an internal donor-free supported catalyst and TiCl$_4 \cdot$ ester complexes. The binding energies the Ti$_{2p3/2}$ peak in the three supported catalysts were almost the same in spite of the difference in the internal donor. The higher values of the binding energy in the TiCl$_4 \cdot$ ester complexes, compared with the supported catalysts, indicated that the TiCl$_4 \cdot$ internal donor complex itself did not exist on the surface of the supported catalysts. The comparison of the binding energies among the supported catalysts after the reaction with triethylaluminium (TEA) showed that the reduction of the titanium species on the supported catalysts proceeded at the same level, regardless of the kind of the internal donor and of the catalyst preparation method. From the results obtained in this study, it was concluded that the internal electron donor existed free from titanium species on the supported catalysts, but the nature of the active sites was affected by the change in the environment through the interaction of the donor with MgCl$_2$. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Internal electron donor; Ziegler catalysts; Binding energy; X-ray photoelectron spectroscopy; TiCl$_4 \cdot$ ester complexes

1. Introduction

MgCl$_2$-supported Ziegler catalysts for the polymerization of olefins have had spectacular success in simplifying the polymerization process and improving polymer quality. For propylene polymerization, high activity and high stereospecificity are required for the catalyst, which has been achieved by the evolution of the supporting technique of titanium compounds on MgCl$_2$ and of the addition of various kinds of Lewis bases as internal and external electron donors [1]. The internal electron donor, such as monoester, diester, and diether compounds, is introduced as an important third component during the catalyst preparation procedure and is almost indispensable to obtain the polypropylene having satisfactory stereoregularity.

Much effort has been devoted to the comprehension of the mechanisms through which an internal donor interacts with other components

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of the catalyst. A complete understanding of the role and the existing state of the internal donor in the catalyst, however, has not been achieved, even though it is of prime importance to consider the mechanism of improving the stereospecificity. There are several contrasting opinions on the role and the states of the internal donors. One opinion is that an internal donor enhances the stereospecificity due to its coordination on a vacancy of the titanium compound [2,3]. Through the results of IR analysis, Rytter et al. claimed that esters can coordinate with both $TiCl_4$ and $MgCl_2$ [4,5]. Busico et al. demonstrated that internal donors have no effect on isospecific active sites and prevent the formation of aspecific active sites when they interact with $MgCl_2$ prior to $TiCl_4$ [6,7]. However, Sacchi et al. indicated that internal electron donors are present in the vicinity of the isospecific active sites [8]. Another explanation is that an internal donor only interacts with the support, by which the amount and the situation of $TiCl_4$ on $MgCl_2$ are regulated to improve the stereospecificity. In our previous studies using FT-IR and thermal analysis [9–11], it was demonstrated that the $TiCl_4 \cdot$ ester complex was decomposed by co-grinding with $MgCl_2$ and that ethyl benzoate (EB) and $TiCl_4$ existed independently, interacting only with $MgCl_2$. As described above, the subjects of the role and the existing states of the internal donor in the $MgCl_2$-supported Ziegler catalysts are still under discussion. One of the main reasons for the uncertainty is that the majority of the experimental information available in the literature comes mainly from detailed analysis of the structure of the polymer product. The undefined results are also considered to arise from the fact that some kinds of internal donors, such as EB, are eluted from $MgCl_2$-supported Ziegler catalyst under the general polymerization conditions [1,2]. The difficulty of direct investigation of the active species on the catalyst, due to the complexity of the constitution, low content of the active sites in the catalyst, high sensitivity to oxygen and moisture in the ambient, etc., is

another cause of the uncertainty. Here, it will be useful to observe directly the states of the titanium species in relation to the internal donor, which can make a significant contribution in understanding the essential character of the catalyst.

In the preceding article, X-ray photoelectron spectroscopy (XPS) was successfully applied to evaluate the oxidation states of the titanium species on the surface of Ziegler–Natta catalysts [12]. The difference in the oxidation states between $TiCl_3$, a $MgCl_2$-supported catalyst, and a triethylaluminium (TEA)-treated supported catalyst was observed in terms of the chemical shift of the $Ti_{2p3/2}$ peak. As far as the binding energy in XPS analysis is concerned, an electron donation to an atom makes the peak shift to a lower energy region because of the increase in the electron density on the atom. Therefore, it can be presumed that the interaction of the titanium species with an internal electron donor leads to the chemical shift due to the change in the electron density on titanium on the catalyst. Thus, the states of the titanium species and its correlation to the internal electron donor are considered to be evaluated in terms of the $Ti_{2p3/2}$ peak by using XPS.

The objective of this study is to obtain the information concerning the states of the titanium species in relation to internal donors and on the mechanism of how an internal donor improves the isospecificity of $MgCl_2$-supported Ziegler catalysts. For that purpose, $MgCl_2$-supported Ziegler catalysts having different internal donors, such as EB and dibutylphthalate (DBP), were prepared using the same procedure. The XPS measurements were performed with the $MgCl_2$-supported Ziegler catalysts, an internal donor-free supported catalyst, $TiCl_4 \cdot$ ester complexes, as well as the supported catalysts after contact with a co-catalyst. These observations make it possible to clarify the influence of the internal donor on the states of the titanium species, that is, whether or not the internal donor interacts directly with the titanium compound in the $MgCl_2$-supported Ziegler catalyst.

2. Experimental

2.1. Materials

Heptane and toluene (Wako Pure Chemical Industries) were used after dehydration by passing through a molecular sieve 13-X column. EB (Wako) and DBP (Wako) were used as internal donors after dehydration by molecular sieves. Anhydrous $MgCl_2$ (donated by Toho Titanium), $TiCl_4$ (Wako), nitrogen (Uno Sanso), propylene (donated by Chisso), and TEA (donated by Tosoh Akzo) were used without further purification. TEA was used as a heptane solution.

2.2. Catalysts and $TiCl_4 \cdot$ ester complexes

Three types of supported catalysts were used in this study. The preparation procedure and Ti content of each supported catalyst are summarized in Table 1. $TiCl_4/EB/MgCl_2$ catalyst, in which EB was cited as an internal donor, was prepared by co-grinding $MgCl_2$ and EB followed by the reaction with $TiCl_4$ [13]. $MgCl_2$ (30 g; 11 m^2/g) and ethyl benzoate (6.5 ml) were placed in a 1 l stainless steel vibration mill pot with 50 balls (25 mm diameter) under nitrogen and ground for 30 h at room temperature. The ground powder (6.1 g) was allowed to interact with $TiCl_4$ (200 ml) in a 500-ml three-necked flask at 90°C for 2 h with stirring under nitrogen, followed by washing with heptane. The $TiCl_4/DBP/MgCl_2$ catalyst was prepared by a procedure similar to that for $TiCl_4/EB/MgCl_2$, except for the use of DBP

in place of EB. The internal donor-free catalyst ($TiCl_4/MgCl_2$) was prepared without an internal donor by co-grinding $MgCl_2$ and $TiCl_4$ according to the method reported previously [14]. Finally, the supported catalysts obtained were washed with heptane or toluene.

Two types of $TiCl_4 \cdot$ ester complexes ($TiCl_4 \cdot EB$ and $TiCl_4 \cdot DBP$) were used in this study as a reference. The complexes were prepared in a manner similar to the previously reported method [10]. A heptane solution of an ester (10 ml, 0.30 mmol/l) was placed in a 50 ml flask, followed by the dropwise addition of $TiCl_4$ heptane solution (10 ml, 0.30 mmol/l) with stirring at room temperature. The complexes were then immediately precipitated as a light yellow powder, which was collected by decantation. The precipitates were washed several times with heptane and dried in vacuo.

The TEA-treated supported catalysts were also employed as samples for the XPS observation. The preparation was performed by the reaction of the supported catalyst (0.5 g) with TEA (150 mmol/l, Al/Ti molar ratio = 20) in heptane at room temperature for 10 min. After the reaction, the TEA-treated supported catalyst was washed several times with heptane and dried in vacuo.

2.3. XPS analysis

The XPS measurements of all the samples were carried out on a PHI 5600 ESCA SYSTEM (Φ PHYSICAL ELECTRONIC) at room temperature. The base pressure in the XPS

Table 1
Characterization of the $MgCl_2$-supported Ziegler catalysts used in this study

Catalyst	Preparation method	Titanium content[a] (mmol-Ti/g-cat.)
$TiCl_4/EB^b/MgCl_2$	Co-grinding $MgCl_2$ and EB, followed by the reaction with $TiCl_4$	0.40
$TiCl_4/DBP^c/MgCl_2$	Co-grinding $MgCl_2$ and DBP, followed by the reaction with $TiCl_4$	0.36
$TiCl_4/MgCl_2$	Co-grinding $MgCl_2$ and $TiCl_4$	0.40

[a] Measured by titration method.
[b] EB: Ethylbenzoate.
[c] DBP: Dibutylphthalate.

chamber was typically about 5×10^{-9} Torr. Monochromic Al Kα radiation (1486.6 eV) was used for the analysis. Survey scans (0–1000 eV BE) and high resolution scans of the Ti$_{2p}$ region were acquired for each sample. The conditions of XPS analysis were described in our preceding paper [12]. The binding energy and full width at half maximum intensity (FWHM) of Ti$_{2p3/2}$ peak were used for the analysis of titanium species on the sample surface. The cause of a chemical shift in binding energy of a photoelectron Ti$_{2p3/2}$ peak is both the change in oxidation state of the titanium species and the charge on the nearest neighbor atoms of the excited titanium atom. Accurate binding energy of the Ti$_{2p3/2}$ peak was determined by referencing to the Au$_{4f7/2}$ peak at 84.0 eV. FWHM was measured to appraise the distribution of oxidation states of the titanium species. The acquisition times of the XPS analysis were about 5 h for the supported catalysts and about 1 h for the TiCl$_4 \cdot$ ester complexes. More than three measurements per sample were made, and the reproducibility of the XPS analysis was confirmed. For each of the XPS spectra reported in the following section, an attempt has been made to deconvolute the experimental curve in a series of peaks that represent the contribution of the photoelectron emission from atoms in different chemical environments. These peaks are described as a mixture of Gaussian and Lorentzian contributions in order to take into consideration the effect of the instrumental error on the peak shape characteristic of the photoemission process.

2.4. Polymerization of propylene

Propylene polymerization was performed with the supported catalyst (1.1 g) and TEA (70 mmol/l, Al/Ti molar ratio = 30) in heptane (300 ml) at 55°C for 30 min. The desired charge of the supported catalyst slurry was added to TEA solution saturated with propylene (1 atm) to start the polymerization. The monomer concentration in the polymerization system was maintained by the flow of monomer through a flow meter system (Laminar Flow Meter: Model 536, Metabo; Micro-pressure transducer: DP45, Validyne) at a rate to match consumption by the polymerization. Thus, the polymerization rate was measured as monomer flow rate by the flow meter system. After the polymerization, the reaction system was quenched with ethanol, then the polymer obtained was washed with a large amount of ethanol containing 5 vol.% of 12 N-HCl and dried in vacuo.

2.5. Measurements of resulting polymer

The molecular weight and molecular weight distributions of the polypropylenes obtained were determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (Tosoh TSK-GEL 3000HHR and TSL-GEL 5000HHR) at 140°C using 1,2-dichlorobenzene as a solvent. ^{13}C-NMR spectra were recorded on a Varian Gemini-300 spectrometer at 120°C on 20% (w/v) solutions in 1,2,4-trichlorobenzene. Benzene-d_6 (10 vol.%) was added for internal lock, and hexamethyldisiloxane was used for internal chemical shift reference.

3. Results and discussion

The XPS analysis was applied in this study to elucidate the existing states of the titanium species, that is, whether or not the titanium species interact directly with the internal donor in the MgCl$_2$-supported Ziegler catalyst. Two types of MgCl$_2$-supported Ziegler catalysts containing different internal donors and an internal donor-free supported catalyst were cited as samples to clarify the influence of the type of internal donor on the states of the titanium species. EB and DBP were employed as internal donors because of their general use in the industrial catalysts, which produce isotactic polypropylene. On the MgCl$_2$-supported Ziegler catalysts containing the internal donor, the tita-

nium species were supported by means of the treatment of the ground powder ($MgCl_2$ and an internal donor) with $TiCl_4$. The internal donor-free catalyst was also prepared as a reference, where $TiCl_4$ was fixed on $MgCl_2$ by grinding. The detailed preparation conditions were adjusted to produce the supported catalysts having similar titanium contents (ca. 0.4 mmol-Ti/g-cat.), as shown in Table 1 and in Section 2.

An XPS survey scan was performed on three types of the supported catalysts for the purpose of elemental analysis. A representative survey spectrum of the supported catalyst is shown in Fig. 1. The constituent atoms of the catalysts (Mg, Cl, Ti, C, O) were observed to exist on the XPS measurable surface, approximately 2 nm in sampling depth. To investigate the states of the titanium species in detail, an XPS narrow scan of the Ti_{2p} region was performed for each catalyst, the typical result of which is shown in Fig. 2(A). The doublet at 458.5 and 464.6 eV is reported to be due to the $2p_{3/2}$ and $2p_{1/2}$ photoelectrons from titanium atoms in $TiCl_4$ in its molecular solid state [15,16]. Thus, the doublet shown in Fig. 2(A) is ascribed to the $2p_{3/2}$ and $2p_{1/2}$ photoelectrons from titanium atoms in the $TiCl_4$ existing on the $MgCl_2$-supported Ziegler catalyst. Shifts in binding energy have a contribution from both the oxidation state and the charge on the nearest neighbor atoms of the excited atom. The chemical shift and the FWHM
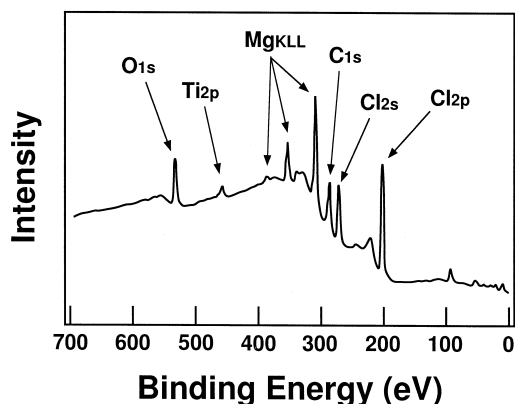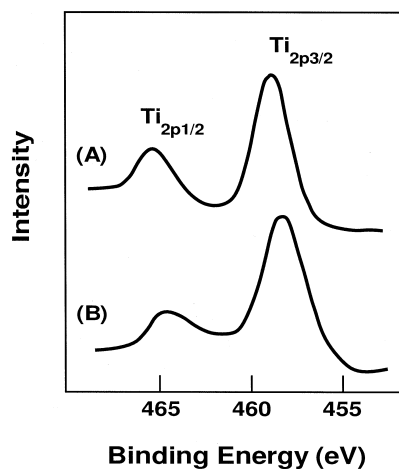
Fig. 2. XPS spectra of Ti_{2p} levels in $TiCl_4/EB/MgCl_2$ (A) and the TEA-treated catalyst (B).

of the $2p_{3/2}$ peak in XPS analysis of Ziegler–Natta catalysts indicate the electron density of the titanium species, namely the oxidation state, and its distribution, respectively [12]. An electron donation to a titanium atom is expected to make the peak shift to a lower energy region and to induce broadening of the FWHM, if the interaction of the titanium species with an internal donor exists in the supported catalysts. However, the values of the binding energies in all the supported catalysts were almost the same, as shown in Table 2 (Run 1–3), indicating that the ester compounds used as internal donors provide little electron donation to the titanium species on the supported catalysts. Thus, it is reasonable to consider that there is no direct

Fig. 1. XPS survey spectrum of $TiCl_4/EB/MgCl_2$.

Table 2
XPS data of the $Ti_{2p3/2}$ level in the supported catalysts and $TiCl_4 \cdot$ ester complexes

Run No.	Catalyst	Binding energy[a] (eV)	FWHM[b] (eV)
1	$TiCl_4/EB/MgCl_2$	458.8	3.0
2	$TiCl_4/DBP/MgCl_2$	458.9	3.1
3	$TiCl_4/MgCl_2$	458.9	2.9
4	$TiCl_4 \cdot EB$ complex	459.1	2.4
5	$TiCl_4 \cdot DBP$ complex	459.2	2.4

[a] Reference: $Au_{4f7/2}$ (84.0 eV).
[b] Full width at half maximum intensity.

interaction of the internal donor with the titanium species on the MgCl$_2$-supported Ziegler catalysts, regardless of the type of internal electron donors.

In the next stage, in order to confirm the consideration, TiCl$_4 \cdot$ EB and TiCl$_4 \cdot$ DBP complexes were employed as samples for XPS measurement. Our previous analytical studies have described that TiCl$_4$ and EB form an equimolar stable complex, suggesting the existence of interaction between TiCl$_4$ and EB [9–11]. Therefore, the influence of the interaction with internal donors on the states of the titanium species could be evaluated from the comparison of the binding energies between the supported catalysts and the complexes. The key concept of this comparison is assuming the formation of the similar complex even on the surface of MgCl$_2$, if the interaction of the titanium species with an internal donor exists in the supported catalysts. The Ti$_{2p3/2}$ peak photoelectrons excited from TiCl$_3$ have a binding energy between 457.0 and 457.6 eV [16]. Whereas, bulk Ti$_2$O$_3$ has the $2p_{3/2}$ peak at 457.5 eV [17]. Titanium atoms in the $3+$ oxidation state, obtained by weak Ar-ion bombardment of the TiO$_2$ single crystal surface, show the $2p_{3/2}$ peak at 457.6 eV [18]. BaTiO$_3$, CaTiO$_3$, PbTiO$_3$, SrTiO$_3$ have been reported to give the $2p_{3/2}$ peaks at 458.5, 458.9, 458.6, 458.8 eV, respectively [19]. The values are similar to that of titanium atoms in TiCl$_4$ in its molecular solid state (458.5 eV) [15,16]. There are no significant differences in the reported binding energies between complexes of Ti^{4+} (or Ti^{3+}) and solid compounds containing Ti^{4+} (or Ti^{3+}). Thus, it seems reasonable to compare the binding energies of the Ti$_{2p3/2}$ peaks between the supported catalysts and the complexes. Based on this consideration, the XPS measurement of the TiCl$_4 \cdot$ ester complexes was conducted. As shown in Table 2, the values of the binding energies in both complexes were apparently higher than those in the supported catalysts, indicating that the states of the titanium species on the supported catalysts were different from those on the complexes.

This is an indication of the non-existence of the TiCl$_4 \cdot$ ester complex itself on the surface of the MgCl$_2$ through physisorption. For the FWHM, the values of the supported catalysts were larger than those of the complexes, which may be due to the broad distribution of the titanium species on the supported catalysts. On the basis of the results, it is also important to bear in mind the electron donation from Mg atoms in the support to the titanium atoms through chlorine bridges in the supported catalysts. This consideration was derived from the fact of the improvement of the activity for ethylene polymerization with the increase in the electron density of titanium chloride by the support [20]. Thus, the feasible explanation for the difference in the binding energies of the titanium peak between the supported catalysts and the complexes is the electron donation from only MgCl$_2$ or from both MgCl$_2$ and the electron donor.

From the results described above, it was verified that the TiCl$_4 \cdot$ internal donor complex did not exist on the supported catalyst surface and that the titanium species accepted electrons from MgCl$_2$. At the present stage, it is difficult to conclude unambiguously the existing states of the titanium species on the MgCl$_2$-supported Ziegler catalysts. If the TiCl$_4 \cdot$ internal donor complex exists through interaction with MgCl$_2$ on the supported catalyst, the titanium species might accept electrons both from MgCl$_2$ and the internal donor. To clarify this point, XPS analysis was performed on the supported catalysts after reaction with TEA. Several authors have demonstrated that a progressive replacement of EB by an aluminium compound takes place during the treatment of a MgCl$_2$-supported Ziegler catalyst containing EB with TEA [1,2]. The behavior of the replacement of the internal donor by TEA is known to be dependent upon the type of internal donor. For example, EB was readily eluted from a MgCl$_2$-supported Ziegler catalyst after the reaction with TEA, while much DBP remained in the catalyst after the reaction [2]. Therefore, the XPS signal of the titanium species after the reaction with

Table 3
XPS data of the $Ti_{2p3/2}$ level in the supported catalysts reacted with TEA[a]

Run No.	Catalyst	Binding energy[b] (eV)	FWHM[c] (eV)	Δ Binding energy[d] (eV)
6	$TiCl_4/EB/MgCl_2$	458.3	3.5	-0.5
7	$TiCl_4/DBP/MgCl_2$	458.4	3.6	-0.5
8	$TiCl_4/MgCl_2$	458.3	3.2	-0.6

[a] The reaction was carried out with TEA ([Al] = 150 mmol/l, Al/Ti molar ratio = 20) at room temperature for 10 min.
[b] Reference: $Au_{4f7/2}$ (84.0 eV).
[c] Full width at half maximum intensity.
[d] Gap in the binding energies between before and after the reaction.

TEA is expected to show different chemical shifts, depending upon the kind of internal donor, if the titanium species interact with the internal donor on the supported catalysts. As can be seen in Fig. 2, the binding energy of the $Ti_{2p3/2}$ peak shifted to the lower binding energy side and the FWHM increased after contact with TEA. Table 3 shows the values of the binding energy and FWHM of the TEA-treated supported catalysts. The Δ binding energy signifies the gap in the values of the binding energies between before and after the reaction with TEA. All the Δ binding energies show negative values, indicating that the reduction of the titanium compound occurs by the reaction of the catalysts with TEA. No difference in the values of the Δ binding energies was observed for three types of the supported catalysts. This means that the reduction of the titanium species proceeds at the same level, even if the degree of the replacement of the internal donor by TEA is dependent upon the type of internal donor. It is

proved that there is no interaction between the titanium species and the internal donor on the surface of the supported catalysts prepared under the conditions used in this study. From these XPS analyses, it was clarified that the titanium species and the internal donor existed independently, each interacting only with $MgCl_2$ in the supported catalyst.

Propylene polymerization with the supported catalysts employed in the XPS analyses was performed to confirm the effect of the internal donor on the active sites and the polymerization behavior. As can be seen in Table 4, only slight differences in polymer yields, number–average molecular weights ($\overline{M}_n$), and isotacticities (mmmm%) of resulting polypropylenes were observed between $TiCl_4/EB/MgCl_2$ and $TiCl_4/DBP/MgCl_2$. However, the polymer

Table 4
Results of propylene polymerization with the $MgCl_2$-supported Ziegler catalysts[a]

Catalyst	Yield (g-PP/ mmol-Ti)	$\overline{M}_n^{[b]} \times 10^{-3}$	mmmm[c] (mol%)
$TiCl_4/EB/MgCl_2$	69.0	3.2	71.9
$TiCl_4/DBP/MgCl_2$	60.4	2.9	72.1
$TiCl_4/MgCl_2$	33.1	0.77	62.8

[a] The polymerization was carried out with TEA ([Al] = 70 mmol/l, Al/Ti molar ratio = 30) at 55°C for 30 min.
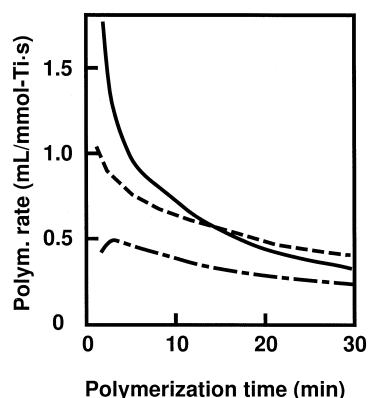[b] Determined by GPC.
[c] Measured by NMR.

Fig. 3. Relationship between polymerization time and polymerization rate with three types of $MgCl_2$-supported Ziegler catalysts; ———: $TiCl_4/EB/MgCl_2$, ---: $TiCl_4/DBP/MgCl_2$, —·—: $TiCl_4/MgCl_2$. The conditions of the polymerization are shown in Table 4.

properties obtained with the supported catalysts containing an internal donor were obviously different from those with the internal donor-free supported catalyst. The polymerization rates of the catalysts measured from the monomer flow rate are shown in Fig. 3. For the polymerization with $TiCl_4/EB/MgCl_2$, the rate at the beginning of the polymerization is quite high, followed by a drastic decay. The curve of the rate with $TiCl_4/DBP/MgCl_2$ is slightly different from that with $TiCl_4/EB/MgCl_2$. The rate with $TiCl_4/MgCl_2$ increases for about the first 5 min and then decays slowly. Thus, different polymerization behavior was observed for the three supported catalysts, even though the values of the binding energies measured by XPS were almost the same. On the basis of the polymerization results combined with XPS study, it is considered that the difference in the polymerization behavior between the supported catalysts is attributed to the different interaction of the internal donor with $MgCl_2$, which regulates the environment of the titanium species on the supported catalysts. That is to say, the nature of the active sites on the $MgCl_2$-supported Ziegler catalysts is considered to be affected by a change in the environment around the titanium species through the interaction of the internal donor with $MgCl_2$.

In this study, the difference in the states of the titanium species between the two types of $MgCl_2$-supported Ziegler catalysts containing different internal donors, the internal donor-free supported catalyst, TEA-treated supported catalysts, the $TiCl_4 \cdot$ ester complexes was evaluated in terms of the values of the binding energy and FWHM of $Ti_{2p3/2}$ peak using XPS. The XPS observations revealed the situation of the interaction between the titanium species, the internal donor, $MgCl_2$ in the supported catalysts as well as the change in the situation after the reaction with TEA. Hence, it is demonstrated that XPS observation has great potential as an effective tool for understanding the states of the active sites and their environments on the $MgCl_2$-supported Ziegler catalysts.

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