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Variation in oxidation state of titanium species on $MgCl_2$-supported Ziegler catalyst and its correlation with kinetic behavior for propylene polymerization

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Abstract

The variation in the oxidation state of the titanium species after reaction with various alkylaluminiums was investigated by X-ray photoelectron spectroscopy (XPS). The reaction of an $MgCl_2$-supported Ziegler catalyst with alkylaluminium was observed to induce a chemical shift to lower binding energy and a broadening of the full width at half maximum intensity (FWHM), depending upon the kind of alkylaluminium. The polymerization kinetics was examined for slurry and stopped-flow polymerization to estimate the relationship between polymerization stages. The catalyst activation and the decay during the polymerization were found to be related to the variation in the titanium species arising from various alkylaluminium compounds. © 1998 Elsevier Science Ltd. All rights resrved.

Keywords: X-ray photoelectron spectroscopy; Oxidation state; Polymerization kinetics; $MgCl_2$-supported Ziegler catalyst

1. Introduction

$MgCl_2$-supported Ziegler catalysts have achieved spectacular success in improving the activity and stereospecificity of the catalyst. The elucidation of fundamental matters concerning the active sites, however, has not been attained, even though the nature of the active sites plays a crucial role in determining the catalyst performance. Further development of the scientific aspects in this area has required basic understanding not only of the nature of the active sites but also of the correlation with polymerization behavior for olefin polymerization. One promising way to clarify this issue will be to combine surface characterization of the catalyst with kinetic investigation of polymerization with the catalyst.

Intensive efforts have been devoted to elucidate the chemical and structural constitution of the active sites responsible for stereospecific polymerization. Several models, which have been proposed to describe the structure of stereospecific active sites on $MgCl_2$-supported Ziegler catalysts, are speculative, based on detailed analysis of the polymer structure produced during polymerization (e.g. [1]). There is no direct proof of the structure of the active sites. In this situation, surface characterization using modern high-performance analytical techniques is thought to give an opportunity to allow direct observation of the active species. Surface science study is known to provide insights into catalytic mechanisms, reacting species of catalysts, reactivity and selectivity of reactions occurring on the surface of a heterogeneous catalyst. From such a point of view, some surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy, have been applied to various types of Ziegler–Natta catalysts [2–4] and their analogues [5,6]. Concerning the surface observation of $MgCl_2$-supported Ziegler catalysts, only a few reports appear in the literature [7–9] because of their inherent properties and experimental difficulties such as the complexity of constitution, low content of active sites in the catalyst, high sensitivity to oxygen and moisture in the ambient atmosphere. These surface studies have generally given limited information concerning the titanium species before their activation with the co-catalyst, the so-called active site precursors.

In our previous studies, the states of titanium species on $MgCl_2$-supported Ziegler catalysts were observed by several methods, such as FT-IR and thermal analysis [10,11], solid-state ^{13}C-NMR [12], scanning Auger electron microscopy [13] and XPS [14,15]. In particular, XPS was applied to analyze the oxidation state and distribution of the

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titanium species on the supported catalysts in terms of the chemical shift and full width at half maximum intensity (FWHM) of the $Ti_{2p3/2}$ peak. The change in the oxidation state induced by reaction with the co-catalyst was detected by XPS [14]. The interaction of the titanium species with internal donors on $MgCl_2$-supported Ziegler catalysts was also evaluated by XPS [15]. From this viewpoint, it is considered that XPS has great potential as an effective tool for understanding the oxidation state and distribution of the titanium species after reaction with the co-catalyst, which are close to the actual working states of the active species.

The key concept of this study is to assume the variation in the oxidation state of the titanium species, depending upon the reactivity of the alkylaluminium used in the catalyst system. The use of a co-catalyst such as triethylaluminium (TEA) as an activating agent is indispensable for olefin polymerization with Ziegler catalysts. The catalyst efficiency is known to be changed by using a different alkylaluminium compound as co-catalyst, as well as by using the same co-catalyst at different concentrations. As far as the active sites are concerned, it is generally accepted that their formation proceeds by alkylation and reduction of the titanium species in the catalyst during the activation reaction with the co-catalyst. In propylene polymerization, $MgCl_2$-supported Ziegler catalyst systems are subject to rapid decay due to the deactivation of the active sites by interaction with the alkylaluminium, at which further reduction of the Ti^{3+} species occurs to a lower oxidation state having no activity for propylene polymerization [1,16,17]. Therefore, it seems reasonable to associate the reactivity of the co-catalyst with the oxidation state of the titanium species formed by the co-catalyst and with the polymerization behavior.

On the basis of this consideration, our approach was based on XPS measurement for the titanium species formed with a variety of alkylaluminiums and on the kinetic study of propylene polymerization with the catalyst systems. The combination of these complementary techniques will provide a profound insight into the relationship between the nature of the active sites on the catalyst and the polymerization behavior.

2. Experimental

2.1. Materials and catalyst

Propylene (donated by Chisso Corp.) was used without further purification. Alkylaluminium, involving triethylaluminium (TEA), diethylaluminium chloride (DEAC), ethylaluminium dichloride (EADC), tri-*n*-butylaluminium (TNBA), tri-*n*-hexylaluminium (TNHA) and tri-*n*-octylaluminium (TNOA), was kindly donated by Tosoh Akzo Corp. and used in heptane solution.

The highly active $MgCl_2$-supported Ziegler catalyst used in this study was prepared according to the method reported previously [18]. $MgCl_2$ (30 g, 11 $m^2\ g^{-1}$) and ethyl benzoate (6.5 ml) were placed in a 1 l stainless steel vibration mill pot with 50 balls (25 mm diameter) and ground for 30 h at room temperature. The ground product (6.1 g) was allowed to interact with $TiCl_4$ (200 ml) in a 500 ml flask at 90°C for 2 h with stirring under nitrogen, followed by washing with heptane. The catalyst was used as a heptane slurry for polymerization. The Ti content of the catalyst was 0.40 mmol Ti/g cat.

2.2. X-ray photoelectron spectroscopy (XPS) measurement

The XPS measurements were carried out on a PHI5600 ESCA System (Φ Physical Electronic) according to the previously reported procedure [14,15]. The samples for XPS measurement were prepared by the reaction with various alkylaluminiums (TEA, DEAC, EADC, TNBA, TNHA, TNOA). The reaction was performed with the supported catalyst (0.38 g) with an alkylaluminium ($[Al] = 150\ mmol\ l^{-1}$, Al/Ti mole ratio = 20) in heptane (20 ml) at room temperature for 10 min. After the reaction, the alkylaluminium-treated catalyst was washed with heptane and dried in vacuo. The catalyst powder obtained was analyzed by XPS. In this study, the sample was always treated under nitrogen to prevent the sample from damage by moisture and oxygen in the atmosphere.

2.3. Propylene polymerization and evaluation of kinetic behavior

Slurry polymerization was typically performed with the $MgCl_2$-supported Ziegler catalyst (0.20 g) and alkylaluminium ($[Al] = 20\ mmol\ l^{-1}$, Al/Ti molar ratio = 50) in heptane (200 ml) at 60°C for 30 min. The desired amount of co-catalyst was added to the propylene-saturated heptane containing the catalyst, at which time the polymerization started. The monomer concentration in the polymerization system was maintained by the flow of monomer through a flowmeter (Laminar Flow Meter: Model 536, Metabo Corp.; Micro-Pressure Transducer: DP45, Validyne Corp.) according to the consumption by the polymerization. The polymerization rate was therefore monitored as the amount of monomer consumption by means of the monomer flowmeter. After polymerization, the reaction system was quenched with ethanol containing 20 vol% of concentrated HCl; then the polymer obtained was washed with a large amount of distilled water and dried in vacuo.

In order to obtain information on the kinetic behavior at the initial stage of polymerization (up to 0.2 s), the results of the stopped-flow polymerization were compared with those of the typical slurry polymerization mentioned above. Stopped-flow polymerization and estimation of kinetic parameters were carried out according to the method reported previously [18–20].

2.4. Measurements of the resulting polymer

The molecular weight of the polymer obtained was determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (TSK-GEL G3000HHR and TSK-GEL G5000HHR) at 140°C using *o*-dichlorobenzene as a solvent. ^{13}C-NMR spectra were recorded on a Varian Gemini-300 spectrometer at 120°C on a 20% (w/v) solution of 1,2,4-trichlorobenzene. Benzene-d_6 (10 vol%) was added as an internal lock, and hexamethyldisiloxane was used for internal chemical shift reference.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy (XPS) measurement

As part of our program of investigating the active sites on $MgCl_2$-supported Ziegler catalysts, XPS was used in this study to observe the variation in the oxidation state of the titanium species formed by the reaction with various alkylaluminiums. In our previous study using XPS [14], the reaction of an $MgCl_2$-supported Ziegler catalyst with TEA used as a standard co-catalyst was found to induce a chemical shift to lower binding energy and broadening of the full width at half maximum intensity (FWHM) of the $Ti_{2p3/2}$ peak. The binding energy decreased with the reaction time (0 min: 458.8 eV; 5 min: 458.5 eV; 10 min: 458.2 eV), indicating the progress of the reduction of the titanium species on the catalyst. It was also suggested that part of the titanium species on the catalyst was reduced by TEA, on the basis of comparison of the values of the binding energy between $TiCl_3$ (457.8 eV), the TEA-treated supported catalyst (458.2 eV) and the supported catalyst without TEA treatment (458.8 eV).

On the basis of the results, XPS measurement was performed for the $MgCl_2$-supported Ziegler catalyst after reaction with six alkylaluminiums (TEA, TNBA, TNHA, TNOA, DEAC, EADC) having different reactivities. The reaction was carried out in heptane at room temperature for 10 min, and the treated catalyst was washed with heptane and dried in vacuo. The values of the binding energy and the FWHMs of the $Ti_{2p3/2}$ peak were used as indexes for the evaluation of the oxidation state of the titanium species and its distribution on the catalyst surface. The binding energy was found to decrease, while broadening of the FWHM was observed by the reaction with alkylaluminium, as can be seen in Table 1. The sample reacting with a highly active co-catalyst, such as TEA, showed lower binding energy and wider FWHM. These results suggest that the variation in the oxidation state of the titanium species is related closely to the reactivity of the alkylaluminium. Here, it is worth while detecting the difference in the titanium species produced by the reaction with various alkylaluminiums through XPS observation.

Table 1
XPS data of $Ti_{2p3/2}$ level in the catalyst after reaction with various alkylaluminiums[a]

Alkylaluminium	Binding energy[b] (eV)	FWHM[c] (eV)
TEA	458.3	3.5
TNBA	458.4	3.4
TNHA	458.5	3.3
TNOA	458.5	3.3
DEAC	458.7	3.2
EADC	458.8	3.2
—[d]	458.8	3.0

[a] Sample preparation was carried out in heptane at room temperature for 10 min ($[Al] = 150\ mmol\ l^{-1}$, $Al/Ti = 20$).
[b] Reference: $Au_{4f7/2}$ (84.0 eV).
[c] Full width at half maximum intensity.
[d] Without alkylaluminium treatment.

3.2. Kinetic study of slurry polymerization and its correlation with the oxidation state of the titanium species determined by XPS

Kinetic study is a useful method of elucidating how polymerization proceeds on the active sites formed by the reaction of the catalyst with the co-catalyst. In this study, a kinetic investigation of propylene polymerization was carried out in order to obtain information on the relationship between the variation in the oxidation state of the titanium species arising from various alkylaluminiums and polymerization behavior. The nature of the active sites—e.g., the oxidation state of the titanium species—is known to vary with polymerization time, which is one of the reasons for the difficulty in obtaining clear information concerning the active sites. With this in mind, the polymerization behavior was investigated at different polymerization stages, namely at the beginning, middle and end of polymerization. Slurry polymerization was performed with the $MgCl_2$-supported Ziegler catalyst using six different alkylaluminiums, the results of which are shown in Table 2. The polymerization behavior was evaluated in terms of the change in the polymerization rate, which was monitored as the amount of monomer consumption by means of the monomer flowmeter. Dependences of the polymerization rate with TEA, DEAC and EADC on the polymerization time are shown in Fig. 1. The initial activity of the polymerization with TEA was very high, followed by a drastic decay, suggesting that the active site precursors are activated at the beginning of the polymerization; then the over-reduction of the activated titanium species proceeds with the polymerization time to give deactivated sites. In the case of polymerization with DEAC, the activity appeared gradually with polymerization time, but it was very low even after polymerization for 30 min. The catalyst system with EADC had no activity, indicating less activation power.

In the next stage, we considered the difference in the polymerization behavior with various alkylaluminiums in detail from the viewpoint of the oxidative state of the

Table 2
Slurry polymerization of propylene with various alkylaluminiums[a]

Alkylaluminium	Yield × 10^{-3} (g PP/mmol Ti h)	$\bar{M}_w$ [b] × 10^{-5}	$\bar{M}_w/\bar{M}_n$ [b]	*mmmm*[c] (%)
TEA	4.3	2.0	9.5	65.1
TNBA	0.97	1.7	6.5	74.9
TNHA	1.1	1.4	6.2	76.4
TNOA	1.1	1.2	5.3	79.0
DEAC	0.21	2.6	4.3	70.2
EADC	trace	—	—	—

[a] [Al]: 20 mmol l^{-1}, Al/Ti: 50, in heptane at 60°C for 30 min.
[b] Determined by GPC.
[c] Determined by ^{13}C-NMR.

titanium species detected by XPS. As described in the previous section, the sample used for XPS measurement was prepared by the reaction of the catalyst with various alkylaluminiums for 10 min. Therefore, the values of the binding energy of the $Ti_{2p3/2}$ peak obtained by XPS are considered to correspond to the oxidation state of the titanium species after reacting with alkylaluminium for 10 min. Here, it is also important to bear in mind the influence of the reactivity of alkylaluminium on both activation and deactivation: the higher the reducing power of the alkylaluminium, the greater the activation and the deactivation. On the basis of this consideration, the states of the active sites may be presumed from the standpoints of the catalyst activation and of the decay during polymerization. The majority of the titanium species is deactivated due to over-reduction after reacting with TEA for 10 min, at which point the value of the binding energy is 458.3 eV. On the other hand, only a part of the titanium species is activated for DEAC and no activation takes place with EADC. The values of binding energy of the samples contacted with DEAC and EADC (458.7 eV and 458.8 eV) are close to that without the reaction with alkylaluminium (458.8 eV). This is an indication that catalyst activation and deactivation during the polymerization are related closely to the oxidation state of the titanium species, depending upon the reactivity of the alkylaluminium used in the catalyst system. In other words, the information obtained by XPS could be applicable for elucidating polymerization behavior during propylene polymerization.

The decay curves of polymerization with four different trialkylaluminiums possessing a different alkyl group are shown in Fig. 2. The slopes of the decay curves at 3 min and 30 min were calculated; these can be regarded as the decay rates at the beginning and end of the polymerization, respectively. As can be seen in Table 3, the decay rate at 3 min decreased with the bulkiness of the alkyl group of the trialkylaluminium. The result indicates that a highly active co-catalyst leads to a high decay rate, because the deactivated sites are produced by over-reduction even at the beginning of the polymerization. On the other hand, a highly active co-catalyst showed a low decay rate at 30 min, suggesting that reducible active site precursors are almost absent in the last stage of polymerization. Thus, the opposite trend of the decay rate with regard to various alkylaluminiums was observed at the different polymerization stages.

3.3. Correlation of the active sites concentration estimated by the stopped-flow method and the oxidation state of the titanium species determined by XPS

With the aim of obtaining a better insight into the formation of the active sites, the influence of various trialkylaluminiums on the kinetic parameters was investigated in

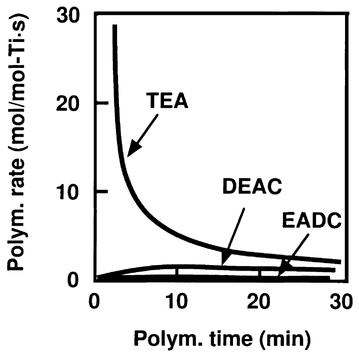

Fig. 1. Decay of polymerization rates with TEA, DEAC and EADC (the conditions of the propylene polymerization are shown in Table 2).

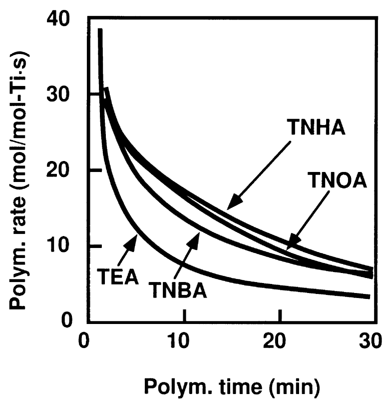

Fig. 2. Decay of polymerization rates with TEA, TNBA, TNHA and TNOA (the conditions of the propylene polymerization are shown in Table 2).

Table 3
Results of decay rate and [C^*] for propylene polymerization with various alkylaluminiums

Alkylaluminium	Decay rate[a] × 10^{-3} (mol/mol Ti s^{-2})		[C^*][b] (mol%)
	3 min	30 min	
TEA	21	0.56	5.6
TNBA	13	1.4	3.6
TNHA	12	1.8	2.7
TNOA	10	2.2	1.6

[a] Decay rate was obtained through slurry polymerization.
[b] [C^*] was estimated from stopped-flow polymerization.

terms of correlation with the oxidation state of the titanium species detected by XPS. The stopped-flow polymerization method [18–20], by which a reaction can be conducted within an extremely short period (ca. 0.1 s), was employed for the determination of the kinetic parameters. The method seems to be most suitable for the kinetic study of olefin polymerization, because the states of the active sites are constant without time-dependent change, and the chain-transfer reaction can be effectively negligible. The important point to note is that the selected information concerning the formation of the active sites can be obtained by using a method in which the over-reduction of the activated titanium species can be ignored. The effect of various kinds of alkylaluminium on the kinetic parameters for the initial stage of propylene polymerization with an $MgCl_2$-supported Ziegler catalyst was recently studied by this method [19]. Here, it is worthwhile considering the relationship between the active site concentrations ([C^*]) and the oxidation state of the titanium species formed with a variety of alkylaluminiums. As shown in Tables 1, and 3, the value of [C^*] increased with the decrease in the binding energy, indicating that the formation of the active sites is directly connected to the reactivity of the alkylaluminium. That is to say, the reason for the low [C^*] for an alkylaluminium with a bulky alkyl group is attributed to insufficient reactivity of the alkylaluminium, resulting in difficulty in activating the active sites precursors at the initial stage of the polymerization. In the cases of polymerization with DEAC and EADC, the catalyst system had no activity at the initial stage of propylene polymerization. The results suggest that the reactivity of DEAC and EADC is not high enough to form active sites from their precursors within the extremely short period.

3.4. Correlation of the structure of the resulting polymer and the oxidation state of the titanium species determined by XPS

For the achievement of more detailed aspects, it may be useful to look more closely at the correlation of the oxidation state of the titanium species with the stereoregularity and molecular weight distributions of polypropylenes obtained by slurry polymerization with various trialkylaluminiums. As can be seen in Tables 1 and 2, the values of the meso pentad fraction (*mmmm*, %) were found to increase in a manner similar to the variation in binding energy, which can be explained from the viewpoint of the reactivity of the alkylaluminium. A decrease in the reactivity of alkylaluminium is considered to depress the withdrawal of a chloride atom from the titanium species, which induces higher stereospecificity. The molecular weight distribution of the resulting polypropylenes was observed to decrease in the following order: TEA > TNBA > TNHA > TNOA, which was proportional to the value of the FWHM. It is considered that the highly active alkylaluminium causes a drastic change in the oxidation state of the titanium species, resulting in the broadening of the distribution of the titanium species on the catalyst surface and of the molecular weight distribution. Thus, the variations in stereoregularity and molecular weight distribution arising from various alkylaluminiums can be evaluated from the values of the binding energy and the FWHM of the $Ti_{2p3/2}$ peak.

4. Conclusions

In this paper, the variation in the oxidation state of titanium species on $MgCl_2$-supported Ziegler catalyst with various alkylaluminiums was investigated through XPS and kinetic approaches. The change in the oxidation state, depending upon the reactivity of the alkylaluminium, could be evaluated by means of the values of the binding energy and the FWHM, using XPS. The kinetic investigation indicated that the variation in the oxidation state arising from various alkylaluminiums was closely related to the polymerization behavior, including the catalyst activation and the decay at different polymerization stages. From this point of view, it was concluded that the information detected by XPS could be regarded as a reliable indicator to consider the variation in the oxidation state of the titanium species at each polymerization stage and its correlation with the polymerization behavior.

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