In-situ multinuclear solid-state NMR spectroscopy under continuous-flow conditions for investigations of Ziegler–Natta catalyzed propene polymerization

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Abstract

Multinuclear (^{1}H, ^{13}C, ^{27}Al) high-resolution solid-state nuclear magnetic resonance (NMR) during the continuous-flow of propene monomer was applied to analyze in-situ propene polymerization on Ziegler–Natta catalysts. A supported Ziegler catalyst activated with triethylaluminum and AA-TiCl$_3$ were employed as catalysts. The time-dependent change in the spectral peak intensities during the propene polymerization with both catalysts was measured using ^{13}C CP MAS (cross-polarization with magic angle spinning) NMR and ^{1}H MAS NMR. The states of the aluminum complex in the catalysts were studied using ^{27}Al MAS NMR, which is sensitive to the coordination and symmetry of the local environment around the aluminum nuclei. Peculiarities of the polymerization kinetics, the crystalline states of the nascent polypropene formed on the catalyst surface, and the state of aluminum coordination and environment during the early stage of the propene polymerization under continuous-flow condition are discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The significance of the heterogeneous Ziegler–Natta catalysts is reflected in the fact that the worldwide market of the polyolefin produced by the catalysts is still growing year by year. For the gas phase polymerization process, which is the most modern and economical one, the chemical reaction occurs when the gaseous reacting species (monomer) interact with the catalyst surface. In order to develop new generations of catalysts with superior properties, it is essential to obtain control over the reaction in a more sophisticated way. Therefore, the understanding of the real time dynamics of the reactions and the time-dependent change in the active species that occur on the heterogeneous catalyst surface are a prerequisite for progress in this field. In the field of surface science, a large number of techniques have been invented and developed because of the necessity for atomic level scrutiny of surface properties. These techniques employ photons, electrons, and ions to determine surface structure, surface composition, and the oxidation states of surface atoms and are done with ever increasing spatial, time, and energy resolutions. However, it has been difficult to detect the real time dynamics of the reactions as well as the cata-

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lyst surfaces, because the high-vacuum environment, which is required for most of the surface analytical techniques, does not allow us to reproduce the reactions occurring under the actual polymerization conditions.

One of the promising methods to study the active species of solid catalysts and chemical processes over these sites is nuclear magnetic resonance (NMR) spectroscopy in its modern version with recording spectra in high magnetic fields and use of special methods to narrow the NMR lines of the solid samples (high-resolution solid-state NMR spectroscopy). Meanwhile, in-situ observation has become the most important method in the spectroscopic studies of heterogeneously catalyzed reactions [1]. Recently, a new approach for the in-situ NMR studies under continuous-flow conditions was proposed and implemented in the field of surface gaseous chemical reactions on solid catalysts, such as various zeolite compounds [2–5]. To perform studies of the heterogeneous Ziegler–Natta catalyzed polymerization, it was necessary to devise a special experimental technique for recording NMR spectra with magic angle spinning (MAS) of samples containing solid catalysts under a controlled atmosphere. In our previous study, a new technique for the continuous monomer flow into the MAS rotor was first developed, which allows the in-situ NMR spectroscopic investigations of the transformation of the monomer to the polymer on a heterogeneous supported Ziegler catalyst [6]. The real-time dynamics of the propene polymerization over the catalyst was successfully analyzed using ^{13}C cross-polarization (CP) MAS NMR under the conditions of the continuous-flow of propene. The information on the crystalline state of the nascent polypropene formed on the catalyst surface in the early stage of polymerization could be obtained at the same time. The important advantage of this technique is the ability to achieve the combination of quantitative information about the real time dynamics of the polymerization and insights into the transformations of the active sites under actual reaction conditions. In this work, we report the application of the in-situ NMR technique under continuous-flow conditions combined with multinuclear (^{13}C, ^{1}H, ^{27}Al) high-resolution solid-state NMR for the investigation of the Ziegler–Natta catalyzed polymerization.

2. Experimental part

2.1. Materials and catalysts

Propene (Takachiho Chemical) and nitrogen (Uno Sanso) were used without further purification. Triethylaluminum (TEA) was kindly donated by the Tosoh Akzo and used as a toluene solution. The supported Ziegler catalyst used in this study was prepared by reacting $TiCl_4$ with a mixture of $Mg(OEt)_2$ and dibutylphthalate (DBP) according to a previously reported method [7,8]. The Ti content of the catalyst was 0.61 mmol Ti/g catalyst. The catalyst was reported to have high activity (245 kg PP/mol Ti) and moderate stereoregularity (*mmmm*=ca. 77%) for the typical slurry polymerization even without an external donor [9]. The activated supported Ziegler catalyst was prepared by the reaction of the catalyst with TEA (Al/Ti=10 or 1) in toluene at room temperature for 10 min. $AA-TiCl_3$ (δ-$TiCl_3 \cdot 0.33AlCl_3$) was donated by the Toho Titanium (activity: 1.11 kg PP/mol Ti, *mmmm*=94.5% for the typical slurry polymerization [9]). The preparation and further handling of the catalysts have been performed using a glove bag filled with pure nitrogen according to the previously reported method [6].

2.2. NMR measurements

The ^{13}C, ^{1}H and ^{27}Al MAS NMR spectra were obtained using a Varian UNITY-400 spectrometer operating at 100.71, 400.49 and 104.35 MHz, respectively, at room temperature with a Varian RT/CP MAS probe. The in-situ NMR investigations were carried out using the gas supply system with the modified MAS NMR probe under continuous-flow conditions according to the previously reported procedure [6]. The ^{1}H MAS and ^{13}C CP MAS spectra were recorded for samples rotating at ca. 3 kHz using 7-mm zirconia rotors. The ^{1}H MAS spectra were obtained with a 30° pulse of 3 μs and a relaxation delay of 1 s. The ^{13}C CP MAS spectra were obtained with a contact time of 500 μs, a 90° pulse of 6 μs, and a relaxation delay of 2 s. The ^{1}H and ^{13}C spectra were referenced relative to external tetramethylsilane (TMS). During the NMR measurements as a function of time, 100 or 200 free induction decays (FIDs) were accumulated for each spectrum. Several blank spectra of the catalyst under

a constant flow of nitrogen (0.2 l/min) have been recorded to check the absence of spectral changes. Next, the nitrogen flow was switched off and propene (0.1 l/min) was pumped through the modified MAS rotor. The propene flow rate was controlled using a flowmeter (Kojima Factory). After the reaction, the propene flow was changed to that of nitrogen again.

The ^{27}Al MAS NMR spectra were recorded for samples rotating at ca. 5 kHz using 7-mm zirconia and silicon nitride rotors. The spectra were obtained with a 12° pulse of 1.75 μs and a relaxation delay of 0.2 s. The chemical shift was referenced to an external standard of a 1 M aqueous solution of $Al(NO_3)_3$ for the ^{27}Al NMR spectroscopy.

3. Results and discussion

The aim of the present study is to apply the in-situ NMR technique of the continuous flowing of a monomer gas combined with multinuclear (^{1}H, ^{13}C, ^{27}Al) spectroscopy for the investigation of the Ziegler–Natta catalyzed polymerization. Much attention is being denoted to the interesting in-situ NMR measurements in Ziegler–Natta catalyzed reactions including chain propagation and transfer reactions. In addition, the multinuclear solid-state NMR investigation makes it possible to elucidate the variation in the crystalline state of the nascent polymer formed in the early stage of polymerization, and the local environment of the aluminum species on the catalyst surface during the polymerization. In this article, attention is confined to the time-dependent change in the spectral peak intensities as a direct monitor of the dynamics of these reactions, which is completely different from not only the general morphological study of polymer powders, but also the typical kinetic study for the polymerization.

3.1. In-situ ^{13}C CP MAS NMR studies of propene polymerization on the activated supported Ziegler catalyst

In a previous solid-state NMR study, we developed a technique for the continuous-flow of a gaseous monomer into the modified MAS rotor containing a heterogeneous supported Ziegler catalyst [6]. The direct use of the design described in the literature [4]

was impossible for studies of high moisture and air sensitive materials, because it implies uncontrolled exposure of the sample to the ambient atmosphere at the beginning of the experiment. This problem was alleviated by the modification of the commercial MAS NMR probe involving the injection glass tube, the Teflon attachment, the Teflon holder, as shown in our previous paper [6], and by the application of glove bags filled with pure nitrogen for the experiment startup, which avoids deactivation of the catalyst. In the first series of experiments, the in-situ NMR spectroscopic technique was employed to monitor the real time dynamics during propene polymerization over Ziegler–Natta catalysts. The supported Ziegler catalyst activated with TEA (2 M, Al/Ti=10), filled in the in-situ MAS rotor, was flushed during the measurements with the propene monomer. Figs. 1 and 2 show the ^{13}C CP MAS NMR spectra of the activated supported Ziegler catalyst recorded before (t=0 min) and after (t>0 min) the start of propene flow. The signals due to the propene monomer are not seen due to the short residence time of the gas in the rotor and signal to noise constrains in Figs. 1 and 2. The ^{13}C CP MAS spectrum obtained at t = 0 min consists of a signal at ca. 10 ppm due to the alkyl groups of TEA, as can be seen in Fig. 1(a). This means that the spectrum of the loaded catalyst exhibits a low intensity line belonging
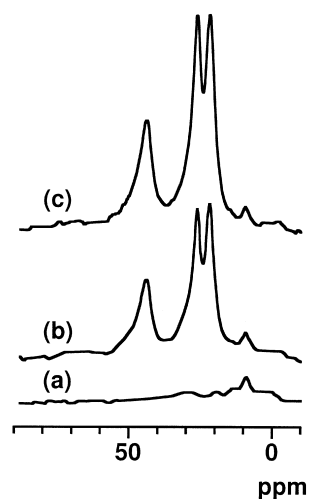

Fig. 1. ^{13}C CP MAS NMR spectra of the activated supported Ziegler catalyst recorded (a) before (t=0) and after (b and c) (t=10 and 60 min) the propene started to flow.
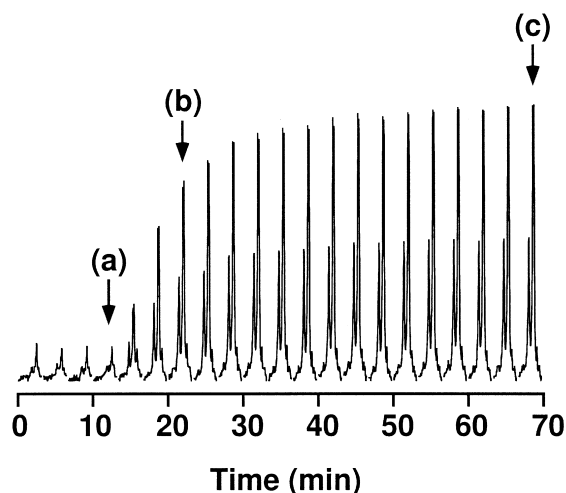
Fig. 2. ^{13}C CP MAS NMR spectra recorded every 200 s under continuous-flow of propene on the activated supported Ziegler catalyst: (a) $t=0$, (b) $t=10$, (c) $t=60$ min, which correspond to Fig. 1.

to the reaction products of the supported Ziegler catalyst with TEA. The spectrum due to the alkyl group was found to remain unchanged for a long time (up to several hours) even after the injection of flowing propene. After the measurement for 10–15 min under the nitrogen flow (until fourth peak in Fig. 2), it was switched off and the flow of propene (0.1 l/min) was started. Each spectrum was accumulated for 200 s. The signals at 44, 26, and 22 ppm attributed to the CH_2, CH and CH_3 groups in polypropene are found to appear upon exposing the sample to the propene flow (Fig. 1(b)). These signals were good agreement with the ^{13}C CP MAS NMR shifts of typical polypropene reported in previous studies [10–12]. During the initial reaction period ($t<10$ min), a rapid growth of the peaks was observed. Then, the spectrum intensity increased gradually up to ca. 30 min, followed by a remaining constant; small changes in intensity could be ascribed to the variation in the probe tuning due to the existence of substantial amount of polypropene in the rotor. The relation of the peak intensities and the propene flow time is considered to corresponding to that of the catalyst activity and the polymerization time for a typical slurry polymerization with a supported catalyst system where the high initial activity is followed by a slow progressive decay. These re-

sults suggest that the time-dependent change in the peak intensities is closely correlated with the characteristics of the catalyst system used. Thus, it is clear that the initial stage of the gas phase polymerization behavior with a heterogeneous supported Ziegler catalyst system can be detected by the in-situ ^{13}C CP MAS NMR under continuous-flow condition.

3.2. ^{1}H MAS NMR studies of polypropene formed on the activated supported Ziegler catalyst

Solid-state NMR is able to provide important information inaccessible by other techniques. In the ^{1}H MAS NMR, the large widths of the proton lines in a rigid solid are caused by homonuclear dipolar couplings. They have long been used to obtain information on the molecular dynamics in polymers as well as other organic materials. Rigid polymer materials, such as polypropene, exhibit broad ^{1}H lines due to its static dipolar couplings [13]. With this in mind, the propene polymerization with the activated supported Ziegler catalyst was investigated by ^{1}H MAS NMR using the continuous-flow conditions at room temperature. Fig. 3 shows the ^{1}H MAS NMR spectra of the sample (a) before and (b) after the in-situ polymerization under continuous-flow condition. The ^{1}H MAS NMR spectrum of the (c) nascent polypropene was obtained by the subtraction of the spectrum of the catalyst in the rotor from the sample spectrum after the in-situ polymerization. The spectrum of the nascent
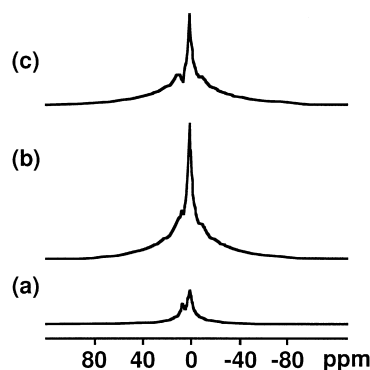

Fig. 3. ^{1}H MAS NMR spectra of the activated supported Ziegler catalyst: (a) catalyst, (b) after in-situ polymerization, (c) nascent polypropene obtained by the substraction of spectrum (a) from spectrum (b).

polypropene is the superposition of a broad peak with a full width at half maximum (FWHM) of about 40 ppm accompanied by a narrow line (FWHM=ca. 5 ppm). The broad pattern reveals that segments still possess a low mobility. This indicates that the nascent polypropene mobility is not high enough to fully reduce the line width. The mass fraction of the integrated narrow peak in the nascent polypropene is less than ca. 35%, suggesting that there are at least two different segments with different mobilities. This low mobility is attributed to the crystalline regions of the isotactic polypropene. Thus, it is considered that the nascent polypropene is composed of a significant amount of crystalline isotactic polypropene. In other words, it has been verified that the in-situ MAS NMR investigation of the activated supported Ziegler catalyst under continuous-propene flow conditions predominantly gave crystalline polypropene, even if the reaction slightly occurs on the catalyst surface. This is in agreement with our previous result for the relaxation times calculated by the ^{13}C CP MAS NMR analysis [6]. This technique is thought to provide an opportunity to allow in-situ observations of the crystallization process of the nascent polypropene formed on the catalyst surface under actual polymerization conditions, which is completely inaccessible by other traditional methods. For the evaluation of the crystalline state and its morphology by typical techniques, a complicated and cumbersome melt-crystallized process from the nascent polymer obtained by polymerization must be involved under appropriate conditions. On the other hand, the application of ^{1}H MAS NMR technique under continuous-flow conditions makes it possible to directly observe the crystalline state of the nascent polymers formed in the early stage of the polymerization on various heterogeneous catalyst systems.

3.3. ^{1}H and ^{13}C MAS NMR studies of propene polymerization on AA-TiCl$_3$

As Ziegler–Natta catalysts, various types of TiCl$_3$-based catalysts have been developed for the propene polymerization. The AA-TiCl$_3$ catalyst, where AA stands for aluminum-reduced and activated, has been developed and used in industrial processes, which is usually considered as the first generation Ziegler–Natta catalyst for polypropene production. It is generally accepted that Ti^{3+} species are almost exclusively present in the TiCl$_3$ system, while a progressive reduction of the Ti^{4+} species is likely to occur to give low oxidative states by the reaction of the supported Ziegler catalyst with alkylaluminum. The activated supported Ziegler catalysts show a greater chemical and structural complexity than the TiCl$_3$-based ones, indicating that the number of parameters potentially able to affect the catalyst performance is higher. Here, in order to confirm the utility of the in-situ solid-state NMR technique for the investigation of various Ziegler–Natta catalysts, ^{1}H and ^{13}C MAS NMR analyses were carried out for the in situ and ex situ propene polymerizations with AA-TiCl$_3$. There were no significant peaks in the ^{13}C CP MAS NMR spectra of AA-TiCl$_3$ (data not shown). The ^{13}C CP MAS NMR spectrum of the sample obtained by ex situ polymerization consists of a broad and low intensity peak, even though the polymerization proceeds on the catalyst surface. This result is apparently different from the one obtained by the activated supported Ziegler catalyst system, in which the signals attributed to the CH$_2$, CH, and CH$_3$ groups in polypropene were clearly observed by ^{13}C CP MAS NMR spectroscopy. It is considered that a spectrum based on the polypropene formed on AA-TiCl$_3$ cannot be detected by ^{13}C CP MAS NMR, which may be due to the heteronuclear C–Ti^{3+} interaction and the excess Ti^{3+} ions that exists in the catalyst. It can be assumed that the inability to see any signals in the spectrum is due to a signal-to-noise problem because the dipolar line broadening experienced by the high gamma ^{1}H nuclei should be greater than that of the low gamma ^{13}C nuclei. At any rate, the direct application of the in-situ ^{13}C CP MAS NMR technique for the AA-TiCl$_3$ catalyzed polymerization is thought to be difficult for the investigation of the kinetics during the early stages of polymerization under continuous-flow conditions.

The in-situ propene polymerization on AA-TiCl$_3$ was used for the analysis by the ^{1}H MAS NMR method. Figs. 4 and 5 present the spectra of AA-TiCl$_3$ recorded before (t=0 min) and after (t>0 min) the start of propene flow. The ^{1}H MAS spectra (until fourth peak in Fig. 5) of the loaded catalyst exhibit a low intensity and broad line, as can be seen in Fig. 4(a), which is attributed to AA-TiCl$_3$. The addition of flowing propene (0.1 l/min) gives a characteristic spectrum including many spinning side bands and a
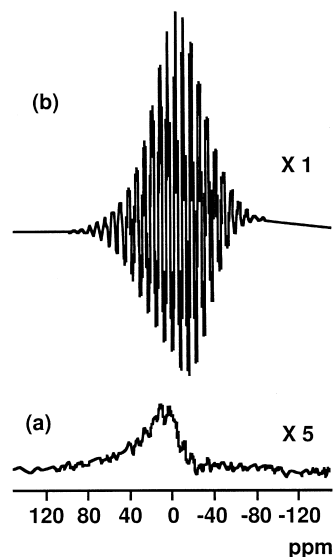
Fig. 4. ^{1}H MAS NMR spectra of AA-TiCl$_3$ recorded (a) before (t=0) and (b) after (t=60 min) the propene started to flow.

very broad line width (Fig. 4(b)). The ^{1}H MAS NMR side band pattern is considered to be caused by the heteronuclear H–Ti^{3+} interaction. The characteristic spectrum of the polypropene obtained by the in-situ polymerization is also presumably due to interference with the paramagnetic Ti^{3+} ions that exist in AA-TiCl$_3$. The signals found after the exposure to the flowing propene indicate the maximum intensity at 0 ppm, which agrees very well the ^{1}H MAS NMR
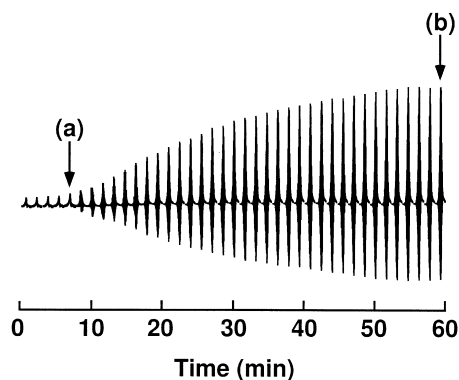

Fig. 5. ^{1}H MAS NMR spectra recorded every 100 s under continuous flow of propene on AA-TiCl$_3$: (a) t=0, (b) t=60 min, which correspond to Fig. 4.

result of the polypropene formed on the activated supported Ziegler catalyst. The increase in the intensity of these lines is observed during ca. 40 min, after which it remained approximately constant, as shown in Fig. 5. Each spectrum was accumulated for 100 s. The initial rate of the activated supported Ziegler catalyst is generally recognized to be higher than that of AA-TiCl$_3$, while AA-TiCl$_3$ has a longer lifetime and stable active species compared with the activated supported Ziegler catalyst. Thus, the difference in the relation of the peak intensity with the monomer flowing time between the activated supported Ziegler catalyst and AA-TiCl$_3$ is considered to be due to the difference in the catalyst properties. Thus, it is substantiated that the kinetics of the propene polymerization on AA-TiCl$_3$ can be observed by ^{1}H MAS NMR, even if the AA-TiCl$_3$ includes large amounts of Ti^{3+} ions, which may seriously interfere with the recording NMR spectra.

3.4. ^{27}Al MAS NMR studies of the catalysts during propene polymerization

^{27}Al NMR is a very promising tool to study the state of the aluminum coordinations, which are sensitive to the coordination and symmetry of the local aluminum nuclei environment [14]. It has been shown for aluminum oxides, zeolites, and aluminosilicates that the position of the ^{27}Al MAS NMR line depends on the aluminum coordination [15]. In the field of heterogeneous olefin polymerization catalysts, the application of ^{27}Al MAS NMR spectroscopy for the investigation of surface species of aluminum-containing compound on MgCl$_2$ has been reported [16,17]. They have demonstrated that the surface complexes of various organoaluminum compounds adsorbed on highly dispersed MgCl$_2$ was identified by ^{27}Al MAS NMR. Taking these points into account, the ^{27}Al NMR investigation was performed using the gas supply system with the MAS probe under continuous-flow conditions. Fig. 6(a) shows the ^{27}Al MAS NMR spectrum of the supported Ziegler catalyst activated with TEA (Al/Ti=10) in the silicon nitride rotor. This spectrum consists of three lines at 0, 30, and 65 ppm. The ^{27}Al MAS NMR spectrum of the activated supported catalyst after the in-situ polymerization (Fig. 6(b)) is similar to that before the polymerization, suggesting that the polymer formation has no influence on
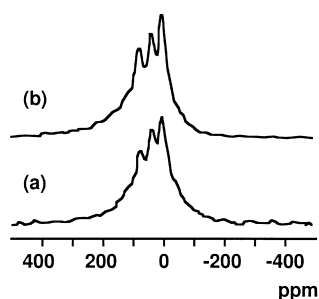
Fig. 6. ^{27}Al MAS NMR spectra of the activated supported Ziegler catalyst in silicon nitride rotor recorded (a) before and (b) after in-situ polymerization.

the aluminum environment in the activated supported Ziegler catalyst. A slight change in the peak pattern during the polymerization process indicates only a minor participation of the NMR-visible aluminum in the deactivation process. This assumption is supported by the ^{13}C CP MAS NMR spectra, as shown in Figs. 1 and 2, where the signals from the alkyls seem to be unchanged during the course of the reaction.

In order to confirm this assumption, the supported catalyst activated with different TEA concentrations (2 M [Al/Ti=10] or 1 M [Al/Ti=1]) at room temperature for 10 min was analyzed by ^{27}Al MAS NMR. The zirconia rotor was used instead of the silicon nitride rotor for the ^{27}Al MAS NMR spectroscopy under continuous-flow conditions, which the aluminum peaks arising from the rotor are present. As can be seen in Fig. 7(a), the lines at 65, 100, and 145 ppm are observed, which are ascribed to aluminum compounds existing in the zirconia rotor. The signal of the zirconia rotor at 100 ppm was used as the standard when the comparison of the peak intensities arising from the change in the aluminum states in the catalyst was carried out. The ^{27}Al MAS NMR spectrum of the activated supported Ziegler catalyst (Al/Ti=10) after the in-situ polymerization (Fig. 7(b)) consists of five lines at 0, 30, 65, 100, and 145 ppm. The Al spectrum of the same sample in the silicon nitride rotor was described in Section 2 to show three peaks. It has been also demonstrated that the spectra of AlEt$_2$Cl/MgCl$_2$ sample and TiCl$_4$/MgCl$_2$/AlEt$_3$ catalyst in the rotor made of poly(methyl metacrylate), which does not contain any own Al species, had all three lines at −3 to 3, 35–38, and 70–80 ppm [16]. This is certainly so in
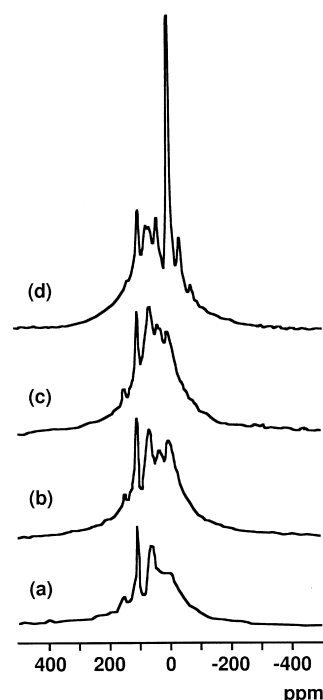

Fig. 7. ^{27}Al MAS NMR spectra of the (a) zirconia rotor, (b and c) the supported Ziegler catalyst activated with TEA (Al/Ti=10 and Al/Ti=1, respectively), and (d) AA-TiCl$_3$.

the case of the line at 65 ppm — thus, there could be the superposition of aluminiumalkylchloride species and Al impurities of the rotor, induced by zirconia. Therefore, it means that the lines at 0, 30, and 65 ppm correspond to the supported Ziegler catalyst activated by TEA. A comparison of the spectra of the samples activated at different TEA concentrations (Fig. 7(b): Al/Ti=10, (c): Al/Ti=1) indicates that the Al/Ti molar ratio has no significant influence on the ^{27}Al MAS NMR chemical shift, while only the intensity of each peak in the spectra shows a slight difference. The relative intensity of the 0 ppm signal increases when the supported Ziegler catalyst was treated with TEA at a higher concentration (Al/Ti=10). Polymerization behavior involving the polymerization rate is known to be remarkably influenced by the aluminum concentration (Al/Ti molar ratio). Thus, it is considered that the slight difference in the NMR-visible aluminum observed is closely connected with the polymerization behavior. Another consideration is that the Al/Ti molar ratio has no influence on the NMR-visible aluminum,

while the number and/or states of the NMR-invisible aluminum, such as the 3-coordinated aluminum, may be changed, resulting in the variation of the polymerization behavior.

A comparison of the supported Ziegler catalyst activated with TEA and AA-TiCl$_3$ was also conducted by ^{27}Al MAS NMR. As shown in Fig. 7(d), a particularly strong signal at 0 ppm is also observed in the ^{27}Al MAS NMR spectrum of AA-TiCl$_3$, which is apparently different from that of the activated supported Ziegler catalyst. This signal correspondences well with the ^{27}Al NMR data for AlCl$_3$ in crystalline form (-3 ppm) and in AlCl$_3$/MgCl$_2$ sample (-2 ppm) [16]. It is considered that there is the simple explanation of these results because the AA-TiCl$_3$ has the composition TiCl$_3$·0.33AlCl$_3$.

The Ziegler–Natta catalyst is highly sensitive to moisture and oxygen in the atmosphere. The reaction of the catalyst with them results in the loss of catalytic activity for olefin polymerization, in which the active sites in the catalyst surface seem to rapidly change due to this reaction. In other words, the state and/or the composition of the active sites is considered to be changed by the exposure to air. If the deactivation reaction is closely correlated with the aluminum compound existed in the vicinity of the active sites, it was inferred that the ^{27}Al MAS NMR spectrum was changed by contact with air due to the change in the aluminum's environment and structure. With this in mind, the activated supported Ziegler catalyst (Al/Ti=10) after the air flow was investigated by ^{27}Al MAS NMR. The ^{27}Al MAS NMR spectrum demonstrates the existence of at least two types (possibly three types) of surface aluminum complexes with different coordination states or environments, as shown in Fig. 8, based on the consideration that the signals at 65, 100, and 145 ppm are due to the zirconia rotor. The intensity of the peak at 0 ppm is found to be increased by contact with air; the ratio of each peak at 0, 65, 100 ppm determined by the deconvolution of the peaks is 34:29:37 wt.% in Fig. 8(a) and 42:26:32 wt.% in Fig. 8(b), respectively. These results suggest that a some of the aluminum compounds are transformed into one another on the catalyst surface or coordination environment of aluminum in this compound became disordered. In this case, it is reasonable to assume the existence of oxygen atoms surrounding the aluminum atoms. When oxygen is present, a chemical shift of 0–10 ppm cor-
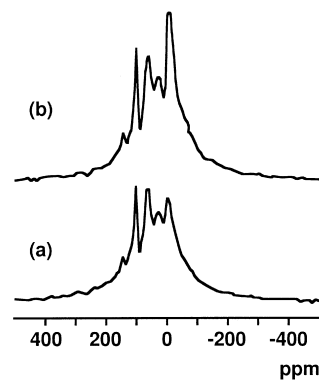

Fig. 8. ^{27}Al MAS NMR spectra of the activated supported Ziegler catalyst in zirconia rotor recorded (a) after in-situ propene polymerization and (b) after air flow for over night.

responds to the octahedral coordination of aluminum, that of 25–35 ppm to pentahedral coordination, and 60–100 to tetrahedral coordination [16]. The precise aluminum coordination state and environment remain as an unclear subject because not only the oxygen but also the chlorine atoms and the ethyl groups exist in the surrounding of the aluminum atoms. However, it must be noted that the change in the relative fraction of the aluminum complexes having different states is confirmed in the catalyst after contacting the air flow. The ^{27}Al MAS NMR study demonstrates the participation of the aluminum compound in the deactivation reaction with oxygen and moisture that exist in air.

Many reports have been published [18,19] regarding the assignment of various aluminum compounds. A comparison of the chemical shifts of AlCl$_3$, AlEtCl$_2$, and AlEt$_2$Cl solutions shows that as an organic ligand replaces an inorganic one in compounds with the same aluminum coordination, the line shifts to a lower field (chemical shift increases). On the other hand, as the aluminum coordination number increases (up to six in crystalline AlCl$_3$), the chemical shift decreases. The reaction of TEA with the supported Ziegler catalyst is thought to produce the AlEt$_2$Cl composition, which shows a strong interaction with the catalyst surface. Taking into account the result of a previous report that the structure of these products is similar to that of AlEt$_2$Cl/MgCl$_2$ [16], the assignments of the ^{27}Al MAS NMR spectra obtained in the study are considered to be as follows. The line at 70–80 ppm is attributed to the 4-coordinated aluminum surrounded

by chlorine atoms or 5-coordinated aluminum with two ethyl groups. The line at 35 ppm can arise from the 6-coordinated aluminum with three ethyl groups in the $(AlEt_2Cl)_n$ chains forming on the $MgCl_2$ surface. The line at 0 ppm most likely corresponds to the 6-coordinated aluminum with 4 chlorine atoms and 2 ethyl groups. In the studies under continuous propene flow conditions, the existence of the oxygen can be negligible in the surrounding of the aluminum atoms because of no chance of contacting the catalyst with air. Therefore, these assignments are considered to be reasonable, even if it is difficult to unambiguously assign the ^{27}Al MAS NMR spectra of heterogeneous Ziegler–Natta catalysts. Further investigations are required to clarify these points.

In this study, the real time dynamics of propene polymerization over Ziegler–Natta catalysts has been investigated using in-situ ^1H and ^{13}C MAS NMR under the conditions of continuous flowing propene. The time-dependent variation in the intensities of the signals attributed to the polypropene formed on the heterogeneous supported Ziegler catalyst could be detected by the in-situ ^{13}C CP MAS NMR under continuous-flow conditions. The ^1H MAS NMR technique also provided in-situ observation of the crystallization state of the nascent polypropene formed on the catalyst surface under actual polymerization conditions. The utility of the ^1H MAS NMR for the kinetic study of propene polymerization on AA-$TiCl_3$ was confirmed in this study, even if the AA-$TiCl_3$ includes large amounts of aluminum and Ti^{3+} ions, which may seriously interfere with the recording of the NMR spectra. The ^{27}Al MAS NMR study of the activated supported Ziegler catalyst indicated that the states of the NMR-visible aluminum were almost constant throughout the polymerization, while the aluminum coordination or environment was changed by contact with air, suggesting the participation of the aluminum compound in the deactivation reaction, and the significant difference in the ^{27}Al NMR signals that was observed between the activated supported Ziegler catalyst and AA-$TiCl_3$. It was demonstrated that the combination of in-situ MAS NMR and the multinuclear (^1H, ^{13}C, ^{27}Al) MAS NMR has a great potential as an effective tool for understanding the Ziegler–Natta catalyzed polymerization. The novel experimental technique described in this contribution would be applicable in studying various types of Ziegler–Natta catalyst systems.

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