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^{27}Al MAS solid state NMR study on coordinative nature of alkyl-Al cocatalysts on a novel SiO_2-supported Ziegler–Natta catalyst for controlled multiplicity of molecular weight distribution

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Abstract

Molecular weight distribution (MWD) is most important factor to determine the mechanical property and processability of polyethylene (PE). The control of MWD is one of the main targets for development of new generation polymerization catalyst. In this work, a novel SiO_2-supported Ziegler–Natta catalyst designed in a molecular level on the silica gel surface modified with linear long alkene chains was developed for ethylene polymerization. The surface modification of silica gel support was performed through the reaction between unsaturated alcohol, 9-decene-1-ol and hydroxyl groups on the SiO_2 surface. This catalyst showed some unique catalytic properties for the control of MWD of PE, which varied significantly from broad and multimodal to narrow and unimodal by solely changing the types of alkyl-Al cocatalyst. The differences in molecular weight (MW) and MWD of the polymers were considered to be caused by different states of active sites in terms of different effects of alkyl-Al cocatalyst. Therefore, the coordinative nature of alkyl-Al should be expected to vary with its structure. The catalysts modified by various alkyl-Al cocatalysts were studied by ^{27}Al magic angle spinning (MAS) solid state NMR method, and the relationship between the coordinative states of Al species and the MW and MWD of PE produced was clarified. Plausible models of active sites formed by various alkyl-Al cocatalysts were proposed as well.

Keywords: Ziegler–Natta catalyst; Alkyl-Al cocatalyst; Ethylene polymerization; Molecular weight distribution (MWD); ^{27}Al MAS solid state NMR

1. Introduction

Nowadays, heterogeneous Ziegler–Natta catalyst as the key member in industrial polyolefin catalysts is still responsible for production of over tens of million tons of polyethylene (PE) each year. The molecular weight (MW) and molecular weight distribution (MWD) of PE are very important for control of proccessablity and mechanical property of the polymers. Even slight difference in MWD, particularly at the head or tail fractions of the distribution, may create strong impact on the processing behavior and final physical properties of the PE materials [1]. A great deal of efforts has been paid for the improvements of polymerization techniques to control the MWD of PE produced with heterogeneous Ziegler–Natta catalysts [2,3]. A broader MWD of polymer is recognized to induce greater flowability in the molten state at higher shear rate, which is the most important factor for the blowing and extrusion processing techniques. MWD of PE is intrinsically determined by the kind of catalyst used. For example, Phillips CrO_x/SiO_2 catalyst can produce PE with an ultra-broad MWD (typically, 10–30), and Ziegler–Natta catalyst usually makes PE with a medium range of MWD (typically, 3–6), while metallocene catalyst creates PE with a narrow MWD (typically less than 3) [4]. The application of metallocene catalyst was hindered by its high cost and poor processibility of PE. The PE products made by Phillips

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catalyst show ideal processability but can be only applied in limited areas due to the existence of residual poisonous Cr species. Therefore, Ziegler–Natta catalyst is still the main industrial catalysts for production of PE. Hence, the achievement of a state-of-the-art control of MWD of PE with broader MWD using heterogeneous Ziegler–Natta catalyst has always been one of the most worthwhile research targets for both industrial and academic fields.

One approach to obtain PEs with broad and/or bimodal MWDs was the employment of a catalyst system comprising two or more different transition metal catalytic species with different propagation, termination, and chain transfer rate constants [5–13], whereas, an optimized control of a broad and/or bimodal MWD together with other important catalytic properties of a hybridized catalyst system is still difficult for an practical application. Another approach to broader MWD, which is being widely applied in most industrial production processes using Ziegler–Natta catalysts, utilized a two- or multi-stage polymerization process, in which each stage produces different MW fractions resulting in PEs with a broad bimodal or multimodal MWD [2,3]. However, such multiple stage systems usually need high investments and high cost for operation compared with a single stage polymerization process. A simple catalyst system giving PEs with controlled narrow and/or broad MWDs without complicated processes is eagerly required from the view point of both industrial application as well as scientific exploration.

In our previous communication, a surface functionalized SiO_2-supported Ziegler–Natta catalyst had been successfully developed [14]. The active sites of this catalyst were extremely stable without deactivation up to 50 h and the MWD of PE can be changed from very narrow and unimodal into very broad and trimodal solely by changing the cocatalyst from diethylaluminumchloride (DEAC) to triethylaluminum (TEA). The alkylaluminum cocatalyst seems play a key role in the determination of MWD of the PEs. It could be expected that the synthesis of PEs having narrow or broad MWD without complicated processes might be realized by using this surface functionalized SiO_2-supported Ziegler–Natta catalyst system. For this purpose, a correlation between the type of cocatalyts used for this catalyst and the coordinative states of Al species on the catalyst surface will be crucial in order to tailor the MWD of PEs. High-resolution solid state nuclear magnetic resonance (NMR) spectroscopy, which is 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, may be the most promising method to study the coordinative states of surface Al species on solid catalysts. The coordinative states of all Al species in terms of four, five or six coordination states on the catalyst surface could be revealed by high resolution ^{27}Al magic angle spinning (MAS) NMR spectrum, which has been fully demonstrated in previous reports on heterogeneous industrial Ziegler–Natta catalysts [15]. In this work, new types of alkyl-Al like ethylaluminumdichloride (EADC), diethylaluminumbromde (DEAB), and diethylaluminumiodide (DEAI) were further used as cocatalyst for ethylene polymerization combined with the novel SiO_2-supported Ziegler–Natta catalyst. Moreover, the coordinative states of surface Al species on this catalyst modified by various alkyl-Al cocatalysts were investigated by ^{27}Al MAS NMR method in order to realize a state-of-the-art design of this catalyst system and MWD of the polymers.

2. Experimental

2.1. Raw materials

Ethylene of research grade (donated by Japan Polychem Co. and Chisso Co.) was used without further purification. $TiCl_4$, Br_2, CCl_4, THF, tetradecane, heptane, toluene (purchased from Wako Pure Chemical Industries Ltd.), 9-decen-1-ol (purchased from Tokyo Kasei Co.), nitrogen (purchased from Uno Sanso Co.), and trimethylchlorosilane (TMCS, purchased from Shin-etsu Chemicals Co.) were used without further purification. Triethylaluminum (TEA), diethylaluminumchloride (DEAC), ethylaluminumdichloride (EADC), diethylaluminumbromide (DEAB), and diethylaluminumiodide (DEAI) (donated from Tosoh Fine Chem. Co.) were used as cocatalyst. Cocatalyst was used as toluene solution. Toluene and heptane were purified by passing through a column of molecular sieves 13 X. Silica gel ES70X made by Crosfield Chemicals was donated by Asahi Kasei Co.

2.2. Preparation of surface functionalized SiO_2-supported Ziegler–Natta catalyst

The specific preparation procedure of the surface functionalized SiO_2-supported Ziegler–Natta catalyst including preparation of SiO_2 with surface functionalized vinyl groups, bromination and lithiation of the vinyl bond, supporting of Ti species, etc., could be found in our previous report [14]. A simplified introduction of the procedure was described as follows.

2.2.1. Preparation of surface functionalized SiO_2

The preparation procedure of the surface functionalized SiO_2 comprised of thermal dehydration of silica gel, functionalization of silica gel surface with 9-decen-1-ol, and masking residual surface hydroxyl groups with TMCS. The concentration of surface hydroxyl groups on silica gel after each step was measured through further reaction with TMCS followed by surface elemental analysis.

2.2.1.1. Dehydration of silica gel. A quartz spouted fluidized bed with a diameter of 35 mm and length of 250 mm was used to dehydrate the silica gel before use. About 15 g of silica gel was put into the spouted fluidized bed under a 200 ml/min flow of dry N_2. The latter was inserted through a perpendicular electronic heater connected with a temperature-controlling programmer. The silica gel was dehydrated at 200 °C for 6 h and subsequently stored in a glass flask under N_2 atmosphere. This dehydrated silica gel was reacted with TMCS to estimate its surface concentration of hydroxyl groups [14]. After the reaction with TMCS, the carbon content of the TMCS-modified silica gel was measured to be 3.7 wt.% by elemental analysis using YANACO CHN CORDER MT-5 instrument. This carbon content of 3.7 wt.% is corresponding to a surface hydroxyl concentration of ca. 1.11 mmol-OH/g-silica under the assumption that TMCS reacted with all of the surface hydroxyl groups on silica gel.

2.2.1.2. Alkylation of silica surface with 9-decene-1-ol. The dehydrated silica gel obtained from the previous stage was further modified with an unsaturated alcohol 9-decene-1-ol according to a reported procedure [16,17]. Dehydrated silica gel (4.0 g) was introduced into a three-neck flask equipped with a Dean–Stark apparatus and dispersed in tetradecane (25 ml). Then, the resulting suspension was heated at 200 °C for 3 h for further dehydration of the reactor system. 9-Decene-1-ol was then added and the resulting suspension was refluxed for 5 h at 200 °C. The solid obtained was separated and washed with heptane (c.a. 100 ml × 10 times). The carbon content for this 9-decene-1-ol-modified silica gel was 10.0 wt.% measured by elemental analysis indicating that 0.94 mmol/g-silica of immobilized 9-decene-1-ol. This means that 0.94 mmol/g-silica of terminal vinyl groups were functionalized on the dehydrated silica gel surface.

2.2.1.3. Masking residual hydroxyl groups with TMCS. There are still about 15.3% of surface residual hydroxyl groups on this surface functionalized SiO_2. In order to further mask these residual unreacted hydroxyl groups, the surface functionalized SiO_2 was further treated by TMCS at 80 °C for 3 h before use for supporting titanium species. After the TMCS masking treatment, the sample showed a carbon content of 10.2 wt.% indicating ca. 90% degree of surface dehydroxylation. The steric hindrance from the immobilized 9-decene-1-ol groups might account for the existence of ca. 10% of residual surface hydroxyl groups.

2.2.2. Catalyst preparation

2.2.2.1. Bromination. The double bonds of the introduced alkyl moieties on the surface functionalized silica gel were brominated to produce bromoalkyl chains [18,19]. The surface functionalized silica gel (4.0 g) was dispersed in carbon tetrachloride (100 ml) under a nitrogen atmosphere. Bromine (3.0 mmol) dissolved in carbon tetrachloride (50 ml) was added dropwise to the resulting suspension at 0 °C. The mixture was then stirred overnight at room temperature under nitrogen atmosphere. The solid obtained was separated and washed with toluene (c.a. 100 ml × 10 times), and dried in vacuum at 100 °C for 6 h.

2.2.2.2. Lithiation and supporting of titanium species. *n*-Butyllithium (3.0 mmol) in tetrahydrofuran (50 ml) was added dropwise into the suspension of the brominated modified silica gel (4.0 g) in tetrahydrofuran (100 ml) at −78 °C, and the mixture was stirred overnight at room temperature under the nitrogen atmosphere so that the bromoalkyl groups could be lithiated [18,19]. After washing with toluene (c.a. 100 ml × 10 times) to remove the unreacted *n*-butyllithium, a toluene solution (50 ml) of titanium tetrachloride (3.0 mmol) was added dropwise into the suspension, and then the resulting mixture was stirred overnight at room temperature. The color of the solid particles gradually changed from pale yellow to pale brown by the addition of titanium tetrachloride. The obtained solid was well washed with toluene (100 ml × 10 times), producing a toluene slurry of the final catalyst. The titanium content of surface functionalized SiO_2-supported catalyst was measured to be 3.1 wt.% by inductive-coupled-plasma spectrometry.

2.3. Ethylene polymerization

The basic procedures for ethylene polymerization described here are similar to those previously reported [14]. Slurry polymerization was performed in a toluene solution (100 ml) with TEA (Al/Ti molar ratio = 100) as the cocatalyst. The polymerization temperature was 60 °C. Calculated amount of TEA was added to the ethylene-saturated toluene solution containing ca. 160–190 mg of catalyst, where the color of the reaction mixture immediately varied from brown to dark green. Ethylene was continuously supplied to maintain the saturation of ethylene in the solution. After the polymerization, the reaction mixture was quenched with ethanol containing 20 vol.% of concentrated HCl, and then the obtained polymer was washed with a large amount of ethanol and dried in vacuum. The alkyl-Al cocatalyst was changed from TEA to DEAC, EADC, DEAB, and DEAI, respectively, for ethylene polymerization under the same procedure mentioned above.

2.4. GPC measurement of polymer

The molecular weight and molecular weight distribution of the polyethylene samples obtained in this study were determined by gel-permeation chromatography (GPC, Waters Alliance GPCV2000CV) with a polystyrene gel column (Shodex UT-806M) at 140 °C using 1,2,4-trichlorobenzene as solvent.

2.5. Catalyst characterization by ^{27}Al MAS solid state NMR

The catalyst was modified by TEA, DEAC, EADC, DEAB, and DEAI, respectively, within a glove bag in nitrogen atmosphere as follows. The catalyst (0.26 mmol Ti) was activated by adding 2.6 mmol of alkyl-Al cocatalyst in 50 ml toluene solution. The Al/Ti molar ratio was controlled at 10, which is lower than that for ethylene polymerization, based on the consideration of the different conditions of the activation of catalyst for solid state NMR characterization and for ethylene polymerization. According to our previous report [20], deactivation of active Ti species would be too severe without the existence of monomer and polymer chains (guard effect to the active sites) during the activation of catalyst for NMR measurement if the same Al/Ti was used as for polymerization [20]. The catalyst slurry added with alkyl-Al cocatalyst was allowed to mix for 30 min at room temperature and then dried in vacuum. The cocatalyst-activated catalyst (ca. 200 mg) was packed into a 7 mm silicon nitride MAS rotor. The surface functionalized silica gel without supporting titanium species was also reacted with TEA and DEAC, respectively, under the same conditions as mentioned above in order to know the difference of coordination between alkyl-Al with titanium species and alkyl-Al with surface of silica gel support. The ^{27}Al MAS solid state NMR spectra were obtained using a Varian UNITY-400 spectrometer operating at 104.35 MHz at room temperature with a Varian RT/CP MAS probe. The ^{27}Al MAS NMR spectra were recorded for samples rotating at ca. 3 kHz using 7 mm silicon nitride rotors. The spectra were obtained with a 12° pulse of 1.75 μs and a relaxation delay of 0.2 s. The strongest ^{27}Al MAS NMR signal of the silicon nitride rotor at 100 ppm was used as the internal standard peak for chemical shift corrections of all spectra obtained from various activated catalysts.

3. Results and discussion

3.1. Multiplicity of MWD of PE induced by different alkyl-Al cocatalysts

Firstly, new types of alkyl-Al like EADC, DEAB and DEAI were further used as cocatalyst, respectively, for ethylene polymerization using the surface functionalized SiO_2-supported Ziegler–Natta catalyst. The results were compared with those of the previous cases using TEA and DEAC [14]. The ethylene polymerization results were shown in Table 1. Those catalyst systems using chlorine-containing cocatalysts (DEAC and EADC) showed higher activity, furthermore, the polymer yield using DEAC as cocatalyst was the highest than those using other cocatalysts. For the conventional $MgCl_2$-supported Ziegler–Natta catalyst system, the polymer yield with TEA was usually higher than that using DEAC. It might be due to the reducing power was too robust, thus some active sites might be deactivated by TEA. The polymer yield with DEAC, DEAB or DEAI was decreased as the halogen atom in the cocatalyst becomes larger. Ratio of these activities with DEAC, DEAB, and DEAI was c.a 4:2:1. From these results, it was considered that the activity of catalyst was related to not only reducing power but also the structure of active sites with respect to the role of cocatalyst.

Table 1
Ethylene polymerization results with surface functionalized SiO_2-supported Ziegler–Natta catalyst

Cocatalyst	Al/Ti[a] (mol/mol)	Activity[b] (g-PE/g-cat.)	M_w[c] (10^3 g/mol)	M_w/M_n[c]
TEA	100	23.8	900	30
DEAC	100	82.6	1.40	1.6
EADC	100	72.4	0.70[d]	1.5[d]
DEAB	100	41.2	477	15
DEAI	100	13.9	968	10

[a] Concentration of alkylaluminum is 230 mmol/l.
[b] Polymerization time is 24 h.
[c] Determination with GPC (Waters Alliance GPCV2000CV) at 140 °C using 1,2,4-trichlorobenzene.
[d] Low-molecular weight fraction.

In Fig. 1, the MWD of PEs obtained from the catalyst system was observed to change from extremely broad to narrow depending on the type of cocatalyst used. In the case of TEA (with three ethyl ligands), a broad and multi-modal MWD ($M_w = 900{,}000$; $M_w/M_n = 30$) was observed, while for DEAC (with two ethyl and one chloride ligands), the MWD of PE was demonstrated to be very narrow and unimodal ($M_w = 1400$; $M_w/M_n = 1.6$). In the case of using TEA, the GPC curve of PE was observed with three peaks. The most lowest-molecular weight fraction of PE might be

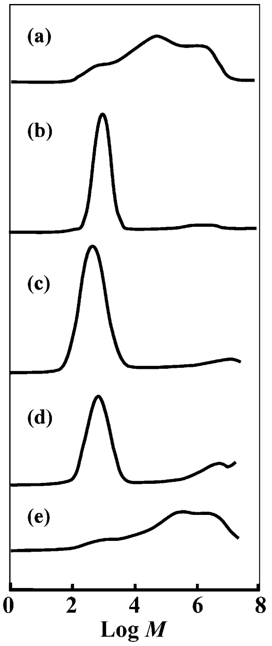

Fig. 1. GPC curves for polyethylenes produced by the surface functionalized SiO_2-supported Ziegler–Natta catalyst using (a) TEA; (b) DEAC; (c) EADC; (d) DEAB or (e) DEAI as cocatalyst with MW and MWD for TEA: $M_w = 900{,}000$; $M_w/M_n = 30$; DEAC: $M_w = 1400$; $M_w/M_n = 1.6$; EADC: $M_w = 34{,}800$; $M_w/M_n = 26$ in which the low M_w peak: $M_w = 700$; $M_w/M_n = 1.5$; DEAB: $M_w = 477{,}000$; $M_w/M_n = 15$ in which the low M_w peak: $M_w = 1000$; $M_w/M_n = 1.65$; DEAI: $M_w = 968{,}000$; $M_w/M_n = 10$. Polymerization conditions: catalyst [Ti] = 0.26 mmol; cocatalyst [Al] = 26 mmol; Al/Ti molar ratio = 100; total slurry volume = 100 ml; ethylene pressure = 1 atm.

derived from DEAC, which could be formed as a by-product of the activation reaction between titanium center and TEA. In the case of using DEAC, only one sharp peak corresponding to the low MW fraction of PE of using TEA was observed with a MWD less than 2. Therefore, it might be speculated that the catalyst system using TEA produced various types of active sites, while the catalyst system using DEAC has uniform type of active sites, which will be discussed in more detail based on solid state NMR results in the next section.

When one more ethyl ligand in DEAC was substituted by another chlorine (in the case of EADC), the MWD of PE was significantly broadened due to the appearance of a broad high molecular fraction ($M_w = 34800$, $M_w/M_n = 26$ in which the low MW peak: $M_w = 700$, $M_w/M_n = 1.5$), whereas, the low MW fraction is still the dominant part in this polymer. As the halogen ligand was changed from Cl to Br and I (corresponding to DEAC, DEAB and DEAI, respectively), consequently the MWD of PE varied from unimodal ($M_w = 1400$, $M_w/M_n = 1.6$) to bimodal ($M_w = 477000$, $M_w/M_n = 15$ in which the low MW peak: $M_w = 1000$, $M_w/M_n = 1.65$) and trimodal ($M_w = 968000$, $M_w/M_n = 10$), respectively. These interesting phenomena were considered to be stemmed from the existence of multiplicity in the nature of active sites with different propagation, termination and chain transfer rates on the surface functionalized SiO_2-supported catalyst combined with different alkyl-Al cocatalysts. One candidate for a reasonable explanation might be related to the real mechanistic roles of alkyl-Al cocatalyst in construction of the active site in heterogeneous Ziegler catalysis, either monometallic or bimetallic active site model, which are still in dispute ever since early 1950's. These results might indicate that DEAC could form stable Al–Ti bimetallic complex with Ti species through two chlorine-bridges which act as active site [21]. Whereas, Al–Ti bimetallic active sites might be difficult to form or unstable when using DEAB or DEAI as cocatalysts. As a result, significant variation of MWD of PEs was observed as changing the alkyl-Al cocatalyst from TEA to DEAC, DEAB and DEAI. Another candidate might be that there mainly exist various kinds of active titanium precursors on the surface functionalized SiO_2-supported catalyst and different cocatalyst might exhibit different ability to activate those different active titanium precursors, as well as different chain transfer ability. A correlation between the types of cocatalyts used for these catalysts and the coordinative states of Al species on these cocatalyst-activated catalysts was established by ^{27}Al MAS solid state NMR and the results will be discussed in detail in the next section.

3.2. Coordinative states of alkyl-Al cocatalysts on activated catalysts

^{27}Al MAS NMR is the most powerful tool for investigation on the coordinative states of surface aluminum species, which are sensitive to the coordination and symmetry of the local environment surrounding the aluminum nuclei [22,23]. In the case of heterogeneous Ziegler–Natta catalysts, the ^{27}Al MAS NMR method could be expected to give useful information relating to the corrdinative states of alkylaluminum cocatalyst.[15,24] In this work, the ^{27}Al MAS NMR technique was applied for the investigation on role and coordinative states of alkyl-Al cocatalyst on surface functionalized SiO_2-supported Ziegler–Natta catalyst in order to further elucidate the mechanistic aspects of the cocatalysts in creating the multiplicity of MWD of PEs. One thing which must be borne in mind is the main difference of existing states of Al species between those remained on the activated solid catalysts and those in the real slurry polymerization system. Considerable amount of Al species resolved in solvent in the real polymerization system is beyond the detection of solid state NMR in this study.

Fig. 2 shows the ^{27}Al MAS NMR spectra of the surface functionalized SiO_2 (without supporting Ti species) reacted with DEAC (Fig. 2A(a)) or TEA (Fig. 2A(b)) and the catalyst activated with DEAC (Fig. 2B(a)) or TEA (Fig. 2B(b)). Two peaks (peaks 1 and 2, marked in Fig. 2) situated at 100 and 145 ppm, respectively, which are ascribed to aluminum compounds existing in the silicon nitride rotor [15], can be observed in all the four spectra. There exist other three peaks (peaks 3, 4, and 5) at around 0, 30, and 65 ppm in all the four spectra shown in Fig. 2, which are corresponding to 6, 5, and 4 coordination aluminum species from the measured samples, respectively [25–27]. The big difference regarding to the relative intensities of these three peaks at 0, 30, and 65 ppm between the surface functionalized silica gel reacted with DEAC or TEA (Fig. 2A) and the catalyst activated with DEAC or TEA (Fig. 2B) could be clearly observed. As it can be seen, for the surface functionalized silica gel reacted with DEAC (spectrum (a) in Fig. 2A), the peaks 3, 4, and 5 show similar relatively low intensities compared with the standard peak 2. For the DEAC-activated catalyst, the relative intensities of peaks 4 and 5 even slightly decreased, meanwhile, the relative intensities of peak 3 significantly increased indicating that the dominant Al species on the DEAC-activated catalyst is four-coordinated and the direct coordination of the DEAC with the silica gel support surface is relatively very weak. For the surface functionalized silica gel reacted with TEA (spectrum (b) in Fig. 2A), the peaks 3, 4, and 5 show also lower intensities compared with the standard peak 2, in which the relative intensity of peak 5 is slightly stronger. For the TEA-activated catalyst, the relative intensities of peaks 3, 4, and 5 significantly increased and all became higher than that of the standard peak 2, meanwhile, the peaks 5 and 4 show the strongest and the second strongest intensity, respectively. These results indicate that the dominant Al species on the TEA-activated catalyst is six- and five-coordinated, which are surface Al species directly coordinated with the surface of silica gel support. The Al species with a state of four-coordination, which is considered to be generated from Al–Ti bimetallic complexing compounds without interaction with the surface of silica gel support, is only the minor Al species in the TEA-activated

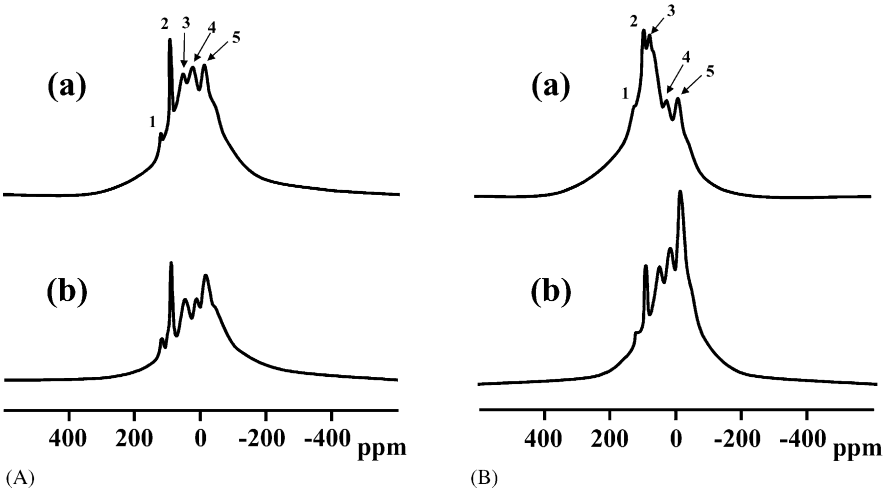

Fig. 2. ^{27}Al MAS NMR spectra of the surface functionalized silica gel support reacted with (A) DEAC (a) or TEA (b), or surface functionalized SiO_2-supported Ziegler–Natta catalyst activated with (B) DEAC (a) or TEA (b). Reaction conditions: catalyst [Ti] = 0.26 mmol, cocatalyst [Al] = 2.6 mmol, Al/Ti molar ratio = 10, total slurry volume = 50 ml, RT.

catalyst. A interesting correlation between the significant variation of coordinative states of Al species with the drastic change of MWD of PEs for the catalyst when cocatalyst was changed from DEAC to TEA could be established as follows. The catalyst/DEAC system with four-coordination Al species as its main Al component seems producing PE with solely narrow MWD at the lowest MW part (spectrum (b) in Fig. 1). The catalyst/TEA system with six-, five-, and four-coordination Al species as the highest, second highest, and lowest Al components, respectively, seems making PE with very broad and trimodal MWD (spectrum (a) in Fig. 1); in which, the weakest peak situated at the lowest MW part.

Fig. 3 shows the ^{27}Al MAS NMR spectra of the catalyst activated with EADC (spectrum (b)), DEAB (spectrum (c)) or DEAI (spectrum (d)) in order to check and confirm the ligand effects from different alkyl-Al cocatalysts. The ^{27}Al MAS NMR spectrum of the catalyst/DEAC (spectrum (a)) was plotted again in Fig. 3 for a clearer comparison. This investigation was carried out to study on effect of the number and atomic size of halogen ligand. According to the polymerization results, the production of PE with the lowest MW was decreased when halogen ligand of the cocatalyst was changed from –Cl (DEAC) to –Br (DEAB) and –I (DEAI) accompanied with increasing relative intensities of other two peaks at the higher MW part (see Fig. 1), while, no obvious variation of MWD except for the emerging of a very weak peak at the highest MW part could be observed when the number of –Cl ligands was changed from one (DEAC) to two (EADC). As it can be seen from Fig. 3, all spectra show five typical peaks at 0, 30, 65, 100, and 145 ppm. For the catalyst reacted with EADC (spectrum (b) in Fig. 3), all the three peaks 3, 4, and 5 show similar relatively intensities in comparison with the catalyst/DEAC system. The only difference between spectrum (b) and spectrum (a) in Fig. 3 is that peak 3 shifted to low field and superposed with peak 2 from the rotor. These evidences imply that the four-coordinated Al species is still the main Al component on the catalyst/EADC system and the direct coordination of the EADC with the silica gel support surface is relatively weak, which is similar to the catalyst/DEAC system, and this could rationalize well why no obvious varia-

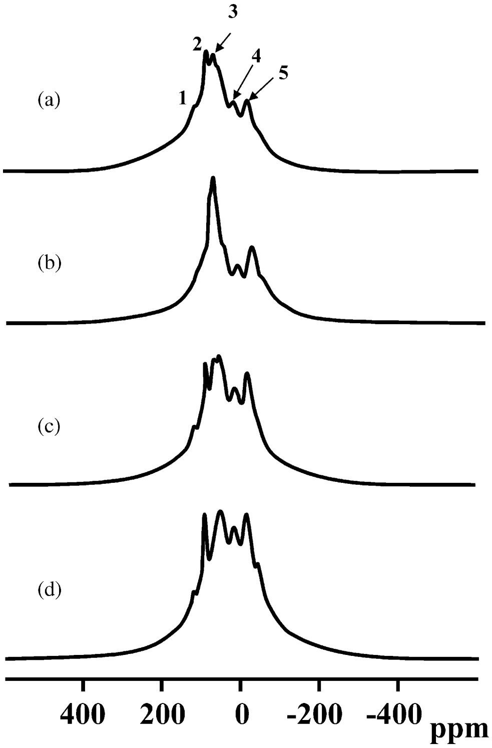

Fig. 3. ^{27}Al MAS NMR spectra of the surface functionalized SiO_2-supported Ziegler–Natta catalyst activated with (a) DEAC; (b) EADC; (c) DEAB; and (d) DEAI. Reaction conditions: catalyst [Ti] = 0.26 mmol, cocatalyst [Al] = 2.6 mmol, Al/Ti molar ratio = 10, total slurry volume = 50 ml, RT.

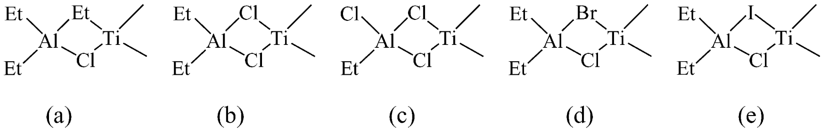

Fig. 4. Plausible structure of Ai-Ti bimetallic active sites formed by halogen containing cocatalysts corresponding to four-coordinated Al species without interaction with the surface of silica gel support (a) TEA; (b) DEAC; (c) EADC; (d) DEAB; and (e) DEAI.

tion of MWD except for the emerging of a very weak peak at the highest MW part was observed when the number of –Cl ligand was changed from one (DEAC) to two (EADC). For the catalyst/DEAB and catalyst/DEAI systems (spectra (c) and (d) in Fig. 3), in both cases peak 3 shows similar relatively intensities in comparison with the catalyst/DEAC system (spectrum (a) in Fig. 3). Whereas, the relative intensities of peaks 4 and 5 obviously increased but still weaker than peak 3 for the catalyst/DEAB system and further increased up to similar intensity level with peak 3 for catalyst/DEAI. These ^{27}Al MAS solid state NMR spectroscopic evidences could explain very well why the production of PE with the lowest MW was decreased when halogen ligand of the cocatalyst was changed from –Cl (DEAC) to –Br (DEAB) and –I (DEAI) accompanied with increasing relative intensities of other two peaks at the higher MW part (see Fig. 1).

So far, the surface functionalized SiO_2-supported Ziegler–Natta catalyst modified by various alkyl-Al cocatalysts was investigated by ^{27}Al MAS solid state NMR method, and a good correlation between the coordinative states of Al species on the activated catalysts and the MW and MWD of PEs produced by the corresponding catalyst/cocatalyst systems has been demonstrated. The six- and five-coordinated Al species are considered to be surface Al species directly coordinated with the surface of silica gel support. The four-coordinated Al species was supposed to be related to active sites making PEs with the lowest MW fraction. One plausible explanation is that the stably coordinated Al-alkyl compound in the instant neighborhood of active Ti species might be much more easily to act as chain transfer agent and subsequently to decrease MW of polymer. The four-coordinated Al species is presumably derived from Al–Ti bimetallic complexing compounds without interaction with the surface of silica gel support. Plausible structure models of Al–Ti bimetallic active sites formed by various alkyl-Al cocatalysts were proposed in Fig. 4. Natta and Mazzanti reported that the stability of the Al–Ti bimetallic complex bridging through two chlorine atoms was higher than that bridging through one chlorine atom and one ethyl group [28]. Moreover, several Al–Ti bimetallic compounds with two chlorine-bridges had been reported to be very stable with well-defined crystalline structure and highly active for olefin polymerization [21,29,30]. Therefore, model (a) in Fig. 4 for catalyst/TEA system should be quite unstable and thus TEA cocatalyst mostly forms six- and five-coordinated Al species through direct coordination with the surface of silica gel support. Therefore, these six- and five-coordinated Al species are not directly associated with active Ti species leaving most of the Ti species to be monometallic. In the case of using TEA, the over-reduction of Ti^{4+} into Ti^{3+} and Ti^{2+} monometallic species will lead to much lower activity and higher MW. [31] In the case of using DEAB or DEAI, the weaker activation power and chain transfer ability will also lead to lower activity and higher MW. The small amount of four-coordinated Al species in catalyst/TEA system might be originated from the by-product DEAC formed from the first activation reaction between the titanium chlorine catalyst and TEA. Models (b) and (c) in Fig. 4 should be quite stable and thus are the main active sites for catalyst/DEAC and catalyst/EADC systems. The stabilities of models (b), (d), and (e) in Fig. 4 were expected to gradually decrease with the increasing of the ligand size (The ion radius of Cl, Br, and I were 1.81, 1.95, and 2.16 Å, respectively) and decreasing of electronegativity from Cl to Br and I. Further experimental and theoretical approaches to the stabilities of Al–Ti bimetallic complexes formed from DEAB and DEAI are still in progress.

4. Conclusion

A novel SiO_2-supported Ziegler–Natta catalyst has been demonstrated to have the capability of creating PE with either narrow and unimodal or broad and multimodal MWD solely through combination with different alkyl-Al cocatalyst. As a purpose for a deeper mechanistic understanding of this phenomenon as well as for tailoring the MWD of polymer through a state-of-the-art design of this catalyst, the catalysts activated by various alkyl-Al cocatalysts were further investigated by ^{27}Al MAS solid state NMR method. A good correlation between the coordinative states of Al species on the activated catalysts and the MW and MWD of PEs produced by the corresponding catalyst/cocatalyst systems has been made clear. The four-coordinated Al species was supposed to be related to active sites making PE with the lowest MW fraction. The four-coordinated Al species is presumably derived from Al–Ti bimetallic complexes formed through two bridges without direct interaction with the surface of silica gel support. The stabilities of these Al–Ti bimetallic complexes were supposed to decrease when one bridge was changed from Cl to Br, I and Et resulting in increasing amount of six- and five-coordinated Al species, which are not directly associated with Ti species.

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