

ZrCl₄-TEA-EASC three-component catalyst for the oligomerization of ethylene: the role of organoaluminum co-catalysts and additives

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Abstract

The catalyst composed of zirconium tetrachloride (ZrCl₄), triethylaluminum (TEA: Et₃Al), and ethylaluminum sesquichloride (EASC: Et₂Al₂Cl₃) was studied for the oligomerization of ethylene. The coordinative interaction of various organoaluminums with Zr and of various additives with Zr and Al was studied by ²⁷Al NMR, ¹H NMR and 2D NMR. The most active catalyst was obtained when TEA was first added to ZrCl₄ and heated above 70 °C for 30 min. Especially the amount of coordinated 2Et₃Al to ZrCl₄ was increased by this method, and the catalytic activity was enhanced. Because stronger coordination of the organoaluminum led to an increase in the electron density at the Zr atom and weakened the strength of the Zr-alkyl bond, the insertion of ethylene into the Zr-alkyl bond was enhanced. The yield and selectivity of the α-olefin was then increased.

An active site for the oligomerization of ethylene is Zr. Therefore, the control of the electron density of Zr is very important. When additives having a small ionization potential (IP) such as tetrahydrothiophene (THT) are coordinated to ZrCl₄, the purity of the α-olefin was improved. This is due to the increase in the electron density of Zr, and the steric hindrance of the bulkier additives to the side reactions of the Zr-alkyl bond. On the other hand, a heterocompound additive having a large electron density is coordinated to an Al atom of TEA and EASC co-catalysts. The ability of various additives to be coordinated to the Al atom was proved to increase in the order of tetrahydrofuran (THF) > THT > thiophene. The formation of a solid polymer by-product also increased in the same order. The solid polymer by-product was considered to form on the over-reduced Zr.

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1. Introduction

A Ziegler type catalyst of triethylaluminum (TEA), Ziegler–Natta type catalysts of Ti and Zr, non-Ziegler type catalysts of a Ni complexes, and Ni or Co oxides supported on alumina or silica-alumina are well-known as catalysts for α-olefin synthesis by the oligomerization of ethylene [1]. Furthermore, an Fe complex catalyst has also been reported to be active in the oligomerization of ethylene [2].

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We found that a zirconium tetrachloride (ZrCl₄)-TEA-ethylaluminum sesquichloride (EASC) three-component catalyst was the best catalyst for the oligomerization of ethylene [3–5]. It was a slurry catalyst composed of a solid phase and a liquid phase, and prepared in a solvent such as cyclohexane.

The catalytic activity was strongly influenced by the method of preparation. Furthermore, the addition of additives to the catalyst influenced the purity of the α -olefin and the amount of the polymer by-products. The catalytic performance was considered to be influenced by the coordination of the organoaluminum co-catalysts to ZrCl₄ and the coordination of the additives to ZrCl₄ or the organoaluminums.

There are many reports on the structure of homogeneous Zr catalysts for the ethylene polymerization based on NMR analysis [6–10]. There are a number of reports on the structure of homogeneous catalysts for the oligomerization of ethylene revealed by NMR spectroscopy. For example, Jones et al. [11] and Oouchi et al. [12], respectively, studied the coordination of ligands and organoaluminum by NMR for homogeneous Zr catalysts containing β -aminoketones and β -diketones.

However, there are few studies on the coordination state in heterogeneous catalysts, three-component for the oligomerization of ethylene. Therefore, we studied the correlation between the performance and the structure of ZrCl₄-TEA-EASC three-component catalyst by NMR spectroscopy.

2. Experimental

2.1. Materials

Cyclohexane as the solvent and the additives were used after drying. ZrCl₄ (Kishida Chemical Co.), TEA and EASC (Tosoh Akzo Co.) were commercial reagents and were used without further purification. For the NMR analyses 99.5% cyclohexane-d₁₂ (Across Organic Co.) and 99.6% benzene-d₆ (Aldrich) were used.

2.2. Preparation of catalyst

The typical method of catalyst preparation is as follows. In a 100 ml Schlenk flask, 50 ml of cyclohexane and 5 mmol ZrCl₄ were added, then 7.8 mmol TEA

was added while stirring. After stirring the solution for 30 min at room temperature (RT), 27.2 mmol EASC was then added to the above mixture and the mixture was heated at 70 °C for 1 h turning dark green. If necessary, the additives (two times the moles of ZrCl₄) were added before heating.

2.3. NMR analysis of catalysts

The NMR analysis was carried out using a JEOL JNM-GX270 type FT NMR (270.05 MHz) by the single pulse non-decoupling method. Two types of NMR tubes (10 mm diameter for ²⁷Al NMR, and 5 mm diameter for ¹H NMR) were used, and the samples were added under dry nitrogen. The chemical shift δ (¹H) in ppm are relative to the standard signal of cyclohexane-d₁₂, δ (¹H) 1.38 ppm. The chemical shift δ (²⁷Al) in ppm are relative to external aqueous Al(NO₃)₃, δ (²⁷Al) 0.0 ppm.

2.3.1. Preparation of sample for ²⁷Al NMR analysis

Catalyst solutions, TEA and TEA added to ZrCl₄ were analyzed by ²⁷Al NMR. A sample of catalyst suspension: 0.7 ml catalyst suspension prepared under various conditions, 1.4 ml cyclohexane and 0.7 ml benzene-d₆ were mixed. The amount of ZrCl₄, TEA and EASC were 0.06, 0.09 and 0.33 mmol, respectively. A sample of TEA: 0.1 mmol TEA, 2.1 ml cyclohexane and 0.7 ml benzene-d₆ were mixed. A sample of TEA-ZrCl₄: 15 mg (0.06 mmol) ZrCl₄, 0.1 mmol TEA, 2.1 ml cyclohexane and 0.7 ml benzene-d₆ were mixed.

2.3.2. Preparation of sample for ¹H NMR analysis

TEA and the additives were analyzed by ¹H NMR and 2D NMR. A sample of TEA: 0.6 mmol TEA, 0.6 ml cyclohexane-d₁₂ and 0.2 ml benzene-d₆ were mixed. A sample of the additives-TEA: 0.08 mmol TEA, 0.6 ml cyclohexane-d₁₂, 0.16 mmol additive and 0.2 ml benzene-d₆ were mixed. A sample of the additives—ZrCl₄: 5.7 mg (0.02 mmol) ZrCl₄ and 0.04 mmol additive, 0.6 ml cyclohexane-d₁₂ and 0.2 ml benzene-d₆ were mixed.

2.4. Oligomerization of ethylene

The oligomerization of ethylene was carried out using a 1000 ml stainless-steel autoclave with magnetic

stirring. A 250 ml solvent of dry cyclohexane was placed in the autoclave under a dry nitrogen atmosphere, and the temperature was raised to 120 °C. The catalyst suspension and dry ethylene were then introduced into the autoclave. During the oligomerization, ethylene was fed at 6.5 MPa, while keeping the autoclave at 120 °C for 1 h. When the autoclave was cooled to ca. 100 °C, an alkaline solution was pumped into the autoclave under ethylene pressure to inactivated the catalyst in order to suppress any decrease in the α -olefin purity during the post-treatment. Then the autoclave was placed in an ice bath to cool, then slowly depressurized, and 10 ml undecane (internal standard for GC analysis) was added.

The inactivated catalyst solution was filtered through a pre-weighed no. 4 filter paper. The filter paper was dried at 140 °C for 24 h and then weighed to determine the amount of the polymer and the wax by-product. The filtrates were analyzed by GC. During the normal workup, the loss of the low boiling point C₄ and C₆ fractions could not be avoided. Therefore, the weight of the oligomer (α -olefin) produced in the C₈–C₃₀ range was analyzed to draw a Schulz Flory [13,14] plot. And, the α -value was calculated to estimate the weight of C₄ and C₆ fraction.

3. Results and discussion

3.1. Preparation method of catalyst and catalytic activity

ZrCl₄-TEA-EASC three-component catalysts were prepared by various methods by changing the addition order of the organoaluminum reagents and the temperature. The influence of the preparation method and catalytic activity was studied [5]. These results are summarized in Table 1. The addition order of two kinds of organoaluminums influenced the catalytic activity. The catalytic activity was the highest when TEA was first added to ZrCl₄ and vice versa. The catalytic activity was around the middle when TEA and EASC were simultaneously added to ZrCl₄. It seems that the extent of coordination of the organoaluminum co-catalyst to ZrCl₄ was dependent on the preparation method, influencing the catalytic activity. The color of the catalyst prepared under these conditions was also different. Furthermore, aging of the catalyst by heating

was necessary in order to produce the high performance. When the aging of the catalyst was not sufficient, the activity and the storage stability of the catalyst decreased. An active catalyst with excellent storage stability was obtained when the catalyst was prepared above 70 °C for 30 min. When the catalyst was heated for a long time at a higher temperature, both the α -value and the average molecular weight increased.

²⁷Al NMR spectroscopy has not been used for the detailed study of organoaluminums. Recently, the $\delta(^{27}\text{Al})$ values for ethylaluminum halides were reported [15–17]. Detailed information on the Al environment under various conditions were obtained by ²⁷Al analysis [18–20]. The chemical shift $\delta(^{27}\text{Al})$ of monomeric Et₃Al with tricoordinated Al atom ranged from 210 to 280 ppm, and the chemical shifts $\delta(^{27}\text{Al})$ of the dimeric 2Et₃Al with tetracoordinated Al atom ranged from 125 to 180 ppm [17,21].

When the organoaluminum co-catalyst was added to ZrCl₄, active species for the oligomerization of ethylene was formed [5,13]. For the ZrCl₄-TEA-EASC catalyst, TEA coordinated to ZrCl₄, and influenced the oligomerization of ethylene. The ²⁷Al NMR spectra of TEA and TEA-ZrCl₄ are shown in Fig. 1. The chemical shift $\delta(^{27}\text{Al})$ of TEA at 156–157 ppm (peak [A]) shows that TEA existed as the dimeric 2Et₃Al (peak [A']) with tetracoordinated Al atom. When TEA was added to ZrCl₄, the peak at 156–157 ppm [A] shifted to 170 ppm [A'] downfield. According to Gaussian curve fitting, it was found that 78% of TEA [A] shifted to [A'] upon the addition to ZrCl₄.

In the organoaluminums, the ²⁷Al nuclei exist in five different nearest-neighbor surroundings as shown in Fig. 2. The chemical shift $\delta(^{27}\text{Al})$ of the type [I] and type [III] are 155 and 170 ppm, respectively, as reported by Čeřny et al. [15]. The downfield shift of $\delta(^{27}\text{Al})$ by adding TEA to ZrCl₄ occurred when the dimeric 2Et₃Al coordinated to ZrCl₄, and was converted to dimeric chlorinated organoaluminum, type [III]. Namely, the $\delta(^{27}\text{Al})$ shift of 2Et₃Al indicated the coordination of TEA to ZrCl₄. On the other hand, when EASC was added to ZrCl₄, the peak of 2Et₂AlCl consisted of EASC shifted downfield. According to Gaussian curve fitting, it was found that 10% of 2Et₂AlCl consisted of EASC shifted upon the addition to ZrCl₄.

Furthermore, the ²⁷Al NMR spectrum of the ZrCl₄-TEA-EASC catalyst prepared under different

Table 1
The method of catalyst preparation and catalytic activity

Catalytic preparation							
Addition order of organoaluminums to ZrCl ₄	First: TEA; second: EASC	First: TEA; second: EASC	First: TEA; second: EASC	First: TEA; second: EASC	First: TEA; second: EASC	First: EASC; second: TEA	First: (TEA + EASC)
Temperature (°C)	50	70	70	80	70	70	70
Aging time (min)	30	30	180	180	60	60	60
Color of catalyst	Green	Dark green	Dark green	Dark green	Dark green	Gray	Green
Catalytic activity							
Days on stream after catalyst synthesis (1 day)							
α-Value	0.58	0.68	0.69	0.75	0.68	0.68	0.68
Catalyst activity (g-oligomer/g-ZrCl ₄)	3000	8150	9320	9300	9500	2300	7810
Days on stream after catalyst synthesis (10 days)							
α-Value	0.62	0.68	0.68	0.73			
Catalyst activity (g-oligomer/g-ZrCl ₄)	4000	8580	9410	9350			

Reaction conditions: 120 °C, 6.5 MPa, 30 min; solvent, cyclohexane; ZrCl₄, 0.2 mmol; EASC, 0.83 mmol; TEA, 0.17 mmol; catalyst concentration, ZrCl₄ 100 mmol/l.

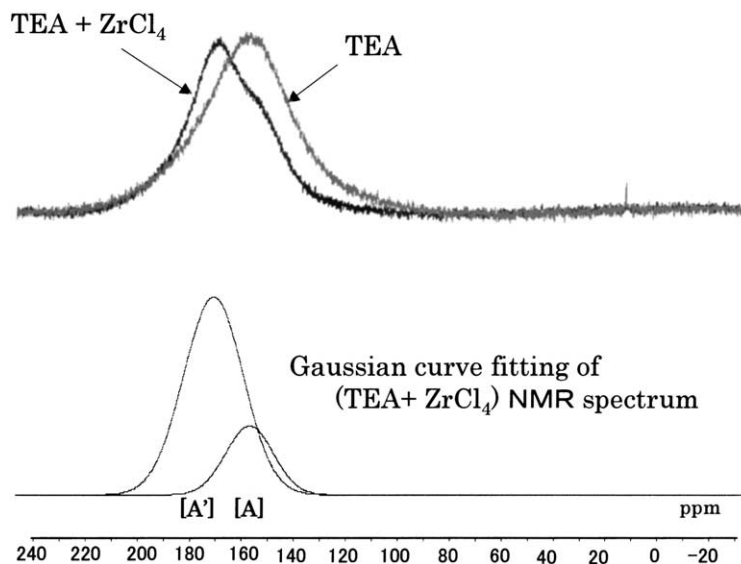


Fig. 1. ^{27}Al NMR spectra of TEA added to ZrCl_4 at 60°C .

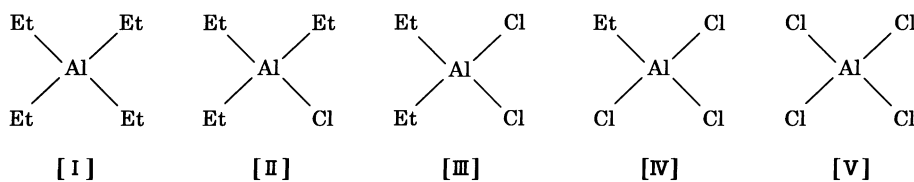


Fig. 2. A Five different nearest-neighbor surrounding of ^{27}Al nuclei of ethylaluminum chlorides.

conditions was analyzed and the influence of ZrCl_4 addition on the chemical shift $\delta(^{27}\text{Al})$ of TEA and catalytic activity are shown in Table 2. With the coordination of TEA to ZrCl_4 , shifts of $2\text{Et}_3\text{Al}$ [A] to [A'] was similarly observed in Fig. 1. The amount of the downfield shift depended on the preparation condi-

tions of the catalyst. When the catalyst was prepared by first adding TEA to ZrCl_4 , and heated at 70°C , the amount of the downfield shift of [A] increased. The amount of TEA coordinated to ZrCl_4 is proportional to the catalytic activity, and Zr seemed to be reduced in the same manner. Therefore, it is considered that

Table 2
The influence of ZrCl_4 addition on ^{27}Al NMR chemical shift at 20°C ^a

Catalysts	$[\text{A}']/([\text{A}]^b + [\text{A}]^c)$	Catalytic activity (g/g- ZrCl_4)
ZrCl₄ + EASC + TEA		
First addition of EASC to ZrCl_4 (50°C , 30 min)	0.75	1200
First addition of TEA to ZrCl_4 (50°C , 30 min)	0.81	3000
First addition of TEA to ZrCl_4 (70°C , 30 min)	0.89	8150

^a Chemical shifts $\delta(^{27}\text{Al})$ in ppm are relative to external $\text{Al}(\text{NO}_3)_3$, $\delta(^{27}\text{Al})$ 0.0 ppm.

^b 170 ppm ($\delta(^{27}\text{Al})$).

^c 156–157 ppm ($\delta(^{27}\text{Al})$).

the catalytic activity increased with the reduction of the active center of Zr by the coordination of the organoaluminum co-catalyst.

3.2. Catalyst composition and catalytic activity

The composition ratio of the ZrCl_4 -TEA-EASC catalyst affected the catalytic activity for oligomer and polymer formations and the product distribution. The catalyst was a heterogeneous slurry system consisting of a solid phase and a liquid phase. The oligomerization of ethylene was postulated to mainly occur on the active site of Zr in the solid phase. Therefore, in order to ascertain the activity of the solid phase and liquid phase, the slurry catalyst was filtered through a glass filter (G5), and the solid part was rinsed three times with solvent to avoid contamination of the organoaluminum in the liquid phase. The amount of aluminum in the solid phase was then measured.

Fig. 3 shows the influence of the TEA/EASC mole ratio on the amount of aluminum in the solid phase and the catalytic activity when the $(\text{TEA} + \text{EASC})/\text{ZrCl}_4$ mole ratio was kept at 7. When the TEA/EASC mole ratio was increased, the Et/Cl mole ratio of the organoaluminums also increased, and the amount of aluminum in the solid phase and the catalytic activity also increased. When ZrCl_4 -TEA and ZrCl_4 -EASC were prepared at 70°C for 1 h, the amount of aluminum in the solid phase of ZrCl_4 -TEA was about 12 times as high as that of ZrCl_4 -EASC. Therefore, the

amount of organoaluminum coordinated to ZrCl_4 is in agreement with the result of the ^{27}Al NMR analysis.

TEA weakened the Zr-alkyl bond because of the low Lewis acidity compared with EASC; therefore, the catalytic activity was enhanced. The influence of the catalyst composition on the amount of polymeric by-product and the α -value is shown in Table 3. In the ZrCl_4 -TEA-EASC three-component catalyst, good performance (high activity and small amount of polymer by-product) was observed when the TEA/EASC mole ratio was 0.3 (Fig. 3 and Table 3).

Fig. 4 shows the influence of the $(\text{TEA} + \text{EASC})/\text{ZrCl}_4$ mole ratio on the amount of aluminum in the solid phase and the catalytic activity, when the TEA/EASC mole ratio was kept at 0.3. When the $(\text{TEA} + \text{EASC})/\text{ZrCl}_4$ mole ratio was increased, the amount of aluminum proportionally increased. However, the catalytic activity leveled off at a $(\text{TEA} + \text{EASC})/\text{ZrCl}_4$ mole ratio of >6 . On the other hand, the α -value of the oligomer decreased (Table 3). As described above, the product distribution can be controlled while maintaining a high activity for the ZrCl_4 -TEA-EASC three-component catalyst.

3.3. Coordination of additives to Zr active site

When the additives were added to the catalyst, the purity of the α -olefin and the formation of solid polymer by-product were influenced. During the oligomerization of ethylene, a competitive insertion reaction

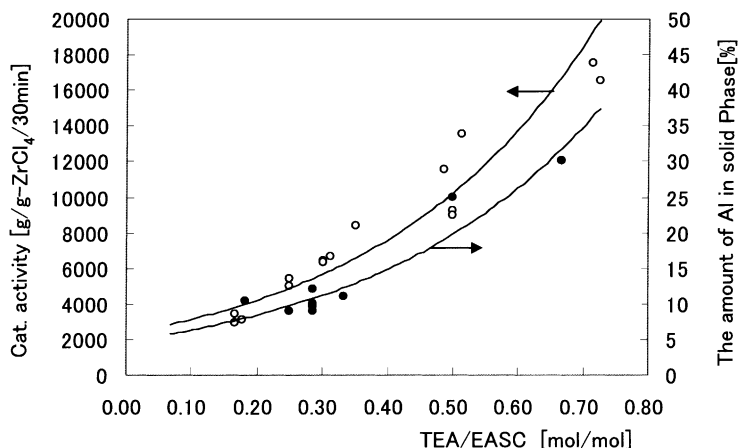


Fig. 3. Catalytic activity and the amount of Al content in solid phase for various TEA/EASC mole ratios $(\text{TEA} + \text{EASC})/\text{ZrCl}_4$ (mole ratio = 0.3).

Table 3

The influence of the catalyst composition on the formation of polymer by-product and α -value

Catalyst composition							
EASC (mmol)	0.47	0.54	0.64	0.31	0.46	0.69	0.85
TEA (mmol)	0.23	0.16	0.06	0.09	0.14	0.21	0.25
TEA/EASC (mole ratio)	0.5	0.3	0.1	0.3	0.3	0.3	0.3
(EASC + TEA)/ZrCl ₄ (mole ratio)	7	7	7	4	6	9	11
Results							
Activity (g/g ZrCl ₄ h)	18.3×10^3	12.2×10^3	6.1×10^3	9.2×10^3	12.3×10^3	11.2×10^3	12.1×10^3
Polymer/oligomer (%)	3.2	0.3	0.3	0.3	0.3	0.2	0.3
α -Value	0.65	0.66	0.65	0.78	0.70	0.61	0.55

ZrCl₄ 0.1 mmol. Reaction conditions: 120 °C, 6.5 MPa, 1 h.

of ethylene and the α -olefin occurred on the Zr active site. When the α -olefin produced by oligomerization was reinserted into the active site of the Zr-alkyl bond, by-products such as branched, vinylidene type, and internal olefins were produced, and the purity of the α -olefin decreased [14]. The C₁₈ α -olefin purity could be calculated by the relative olefin concentration using Eq. (1), because the by-products in the C₁₈ α -olefin were produced by the insertion of the C₄–C₁₆ α -olefin into the Zr-alkyl bond.

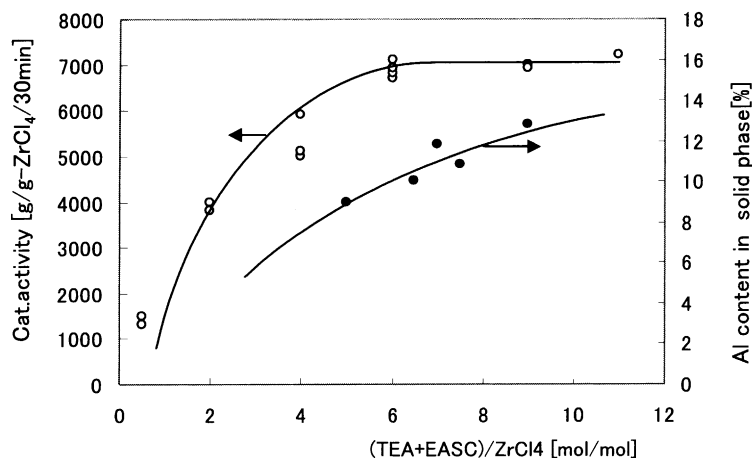
$$C_{18} \alpha\text{-olefin purity} \propto \frac{C_2}{\sum_{n=4}^{16} f_n C_n} \quad (1)$$

where C₂ is the amount of ethylene dissolved in liquid phase (mol); C_n the amount of α -olefins produced with a carbon number of n (mol); f_n the reactivity factor of α -olefin with carbon number of n, f₄ = 8.8×10^{-3} ,

$$f_6 = 4.5 \times 10^{-3}, f_8 = 2.6 \times 10^{-3}, f_{10} = 1.8 \times 10^{-3}, f_{12} = 1.2 \times 10^{-3}, f_{14} = 1.0 \times 10^{-3}, f_{16} = 0.8 \times 10^{-3}.$$

When the relative olefin concentration ($C_2 / \sum_{n=4}^{16} f_n C_n$) was 333.3, the purity of the C₁₈ α -olefin is plotted against the ionization potential (IP) of additives as shown in Fig. 5. There was a good correlation between the IP of these additives and the α -olefin purity. It was shown that the purity of the α -olefin increased upon adding additives with a low IP to the catalyst. When the third component was added to the catalyst as an additive, the purity of the α -olefin and the formation of a polymer by-product during the oligomerization of ethylene were remarkably affected by the electronic properties of these additives [22].

The ¹H NMR analysis was then carried out in order to clarify the influence of the additives on the catalyst. The following compounds, which had a different

Fig. 4. Catalytic activity and Al content in solid phase for various (TEA + TEA)/ZrCl₄ mole ratios TEA/EASC (mole ratio = 0.3).

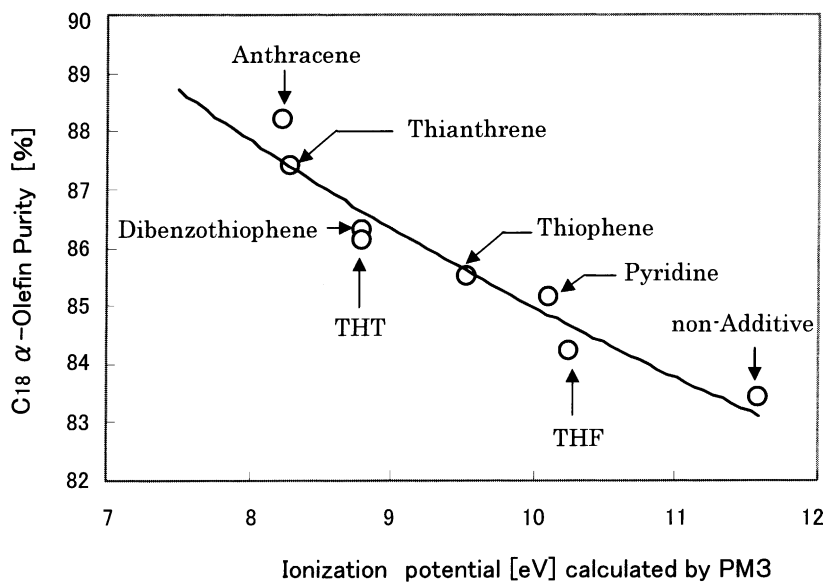


Fig. 5. The influence of additives on the purity of the α -olefin.

IP and electron density (CD) of the heteroatoms, were used as standard additives: thiophene (IP; 9.54, CD; 5.696); tetrahydrothiophene (THT; IP; 8.79, CD; 6.042), and tetrahydrofuran (THF; IP; 10.26, CD; 6.268). The α -values of the IP and electron density were calculated by the molecular orbital calculation PM3 method using MOPAC 97. These additives were added to $ZrCl_4$, and the chemical shift $\delta(^1H)$ was measured. The deviation in the chemical shift of the additive protons is shown in Table 4. An appreciable deviation was observed with thiophene and THT. The deviation was more remarkable at 70 °C than at room temperature. These deviations of the chemical shifts $\delta(^1H)$ were caused by the coordination of these additives to $ZrCl_4$. The deviation in the chemical shift of THF is negligibly small even at 70 °C. From these results, it was concluded that the extent of coordination to $ZrCl_4$ increases in the order of THF (IP; 10.26) \ll thiophene (IP; 9.54) \leq THT (IP; 8.79). The coordination tendency of the additives to $ZrCl_4$ increased with a decrease in the IP and an increase in the temperature. It is thought that a compound having a high IP such as THF could hardly coordinate to $ZrCl_4$. Actually, when THF was added to $ZrCl_4$, no color change was observed. When polycyclic compounds with a small IP such as biphenyl and fluorene were added

to the $ZrCl_4$, deviations in the chemical shifts $\delta(^1H)$ were also observed.

When the additives with an S atom such as THT and thiophene coordinated to $ZrCl_4$, the Hb peak shifted

Table 4

The shift in the 1H NMR signal of additives by the coordination to $ZrCl_4$

	Blank	20 °C	δ	70 °C	δ
Thiophene					
Ha	6.82	6.89	-0.07	6.91	-0.09
Hb	6.93	7.03	-0.1	7.07	-0.14
THT ^a					
Ha	1.65	1.65	0	1.7	-0.05
Hb	2.61	2.74	-0.13	2.78	-0.17
THF ^b					
Ha	1.83	1.84	0	1.86	-0.03
Hb	3.5	3.51	-0.01	3.53	-0.02

Chemical shifts $\delta(^1H)$ in ppm are relative to cyclohexane- d_{12} , $\delta(^1H)$ 1.38 ppm.

^a Tetrahydrothiophene.

^b Tetrahydrofuran.

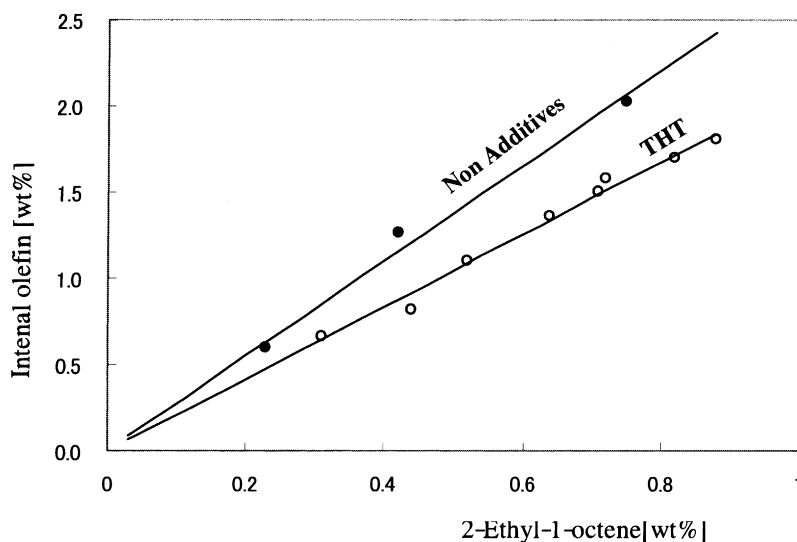


Fig. 6. Influence of additives on the formation of by-products in C10 α -olefin.

significantly downfield. These downfield shifts are considered to be due to the paramagnetic anisotropy effect of Zr as described by Maruya et al. [23]. The downfield shift of the adjacent proton for THT and thiophene from Table 4 seems to be due to its coordination through the S atom, because the shift of the H_b proton was large.

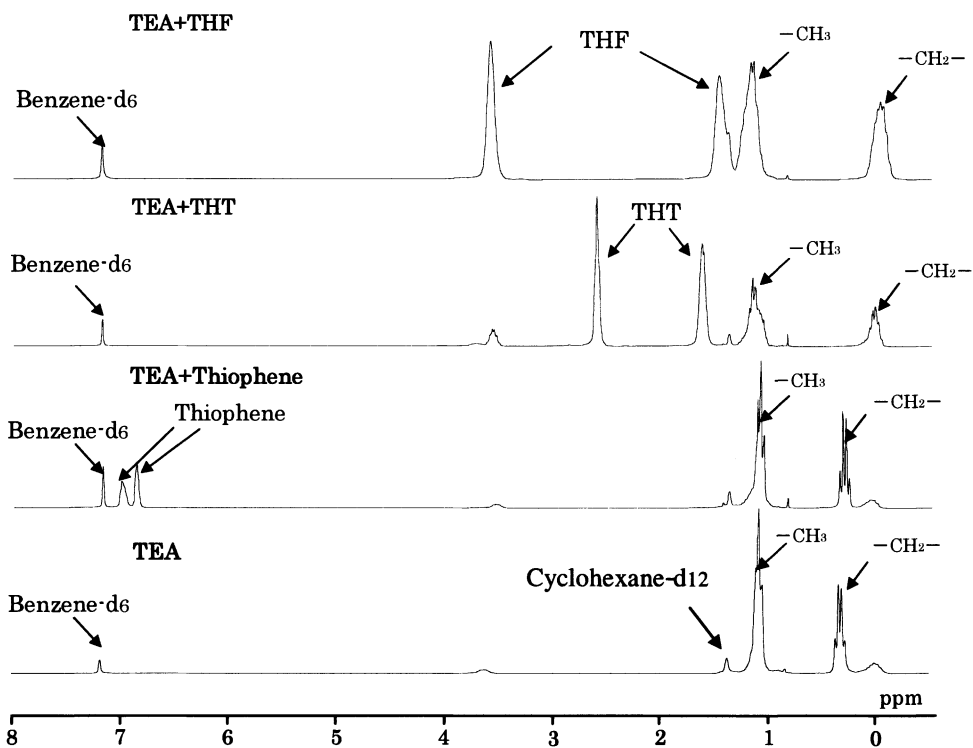
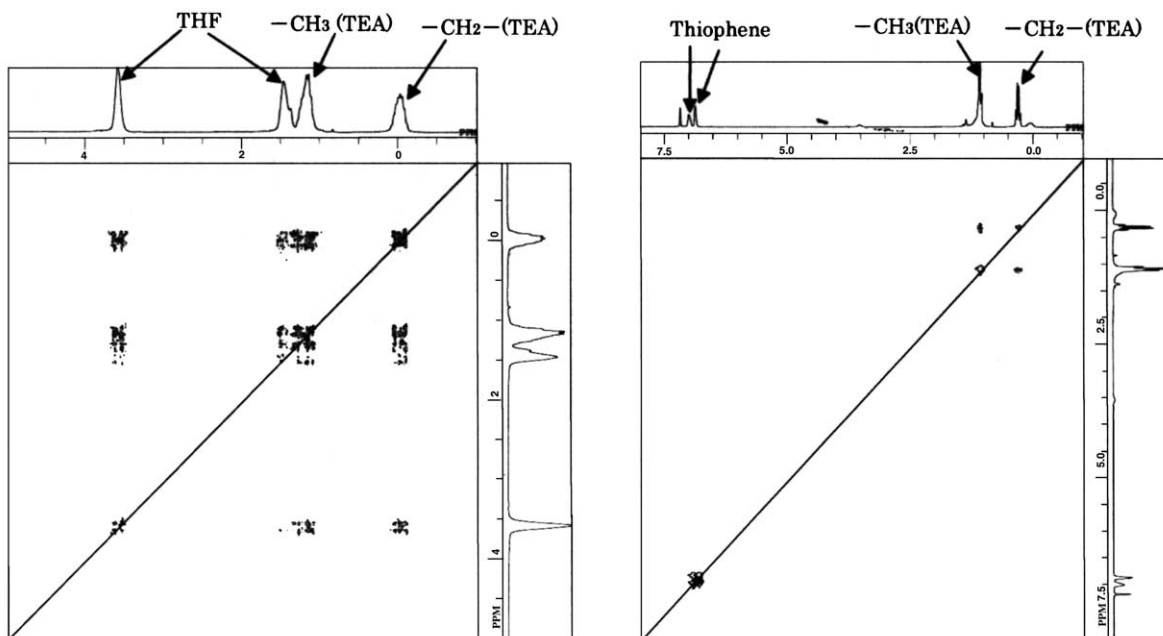
When a bulky additive with a low IP was added to the catalyst, the amount of internal olefins significantly decreased and the purity of the α -olefin increased as shown in Fig. 6. The internal olefin was formed by the anti-Markovnikov type insertion of 1-butene [22]. This was accompanied with the improvement in the purity of the α -olefin due to the inhibition of insertion of the α -olefin into the Zr-alkyl bond mainly based on the steric hindrance of the bulky additives. Especially, the anti-Markovnikov insertion of 1-butene was likely to be inhibited by steric hindrance; therefore, the amount of by-product was small.

3.4. Coordination of additive to organoaluminum

When heterocompounds with a high electron density of the heteroatoms were added to the catalyst, the formation of a polymer by-product increased in the oligomerization of ethylene. Thiophene, THT, and THF were added to TEA, and the chemical shift $\delta(^1\text{H})$

of TEA and the additive protons were measured. These results are shown in Fig. 7. When thiophene was added to TEA, no deviation in the TEA protons was observed. However, a comparable amount of shift was observed when THT and THF were added to TEA; the methyl proton of TEA shifted downfield, and the methylene proton shifted upfield. The shift of TEA was caused by coordination of the additive. However, the shift in the THT proton was small in comparison with that of the THF proton. As described above, the extent of coordination of the additive to the organoaluminum increased in the order of thiophene (CD; 5.696) < THT (CD; 6.042) < THF (CD; 6.268). The order of the coordination tendency of the additive matched the increasing order of the electron density of the heteroatom.

The interaction of the additive and TEA was confirmed by the 2D-NMR COSY spectra. Fig. 8 shows the 2D-NMR COSY spectra when THF and thiophene were added to TEA. A strong interaction between the protons of THF and TEA was observed, indicating that THF coordinated to TEA. On the other hand, no interaction of the thiophene protons with the TEA protons was observed. By analysis of the 2D-NMR COSY, it was also confirmed that the extent of interaction between TEA and each additive was in the order of thiophene <

Fig. 7. ^1H NMR spectra of TEA in the presence of additives at 70°C .Fig. 8. 2D ^1H NMR spectra of THF and thiophene with TEA at 70°C .

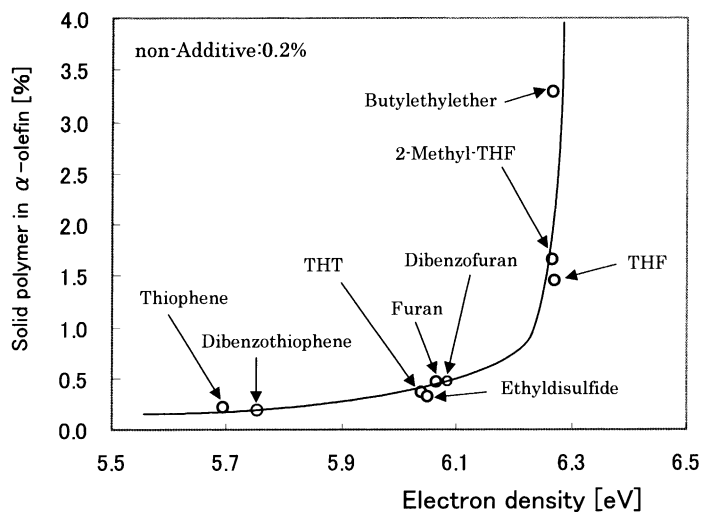


Fig. 9. The formation of polymer vs. electron density of heteroatom, additives/organoaluminums = 2/1 (mol/mol).

THT < THF. This coincides with the relationship in Fig. 7.

From these results, when heterocompounds with a high electron density of the heteroatom such as THF are added to the catalyst, the additive will coordinate to the Al atom of the organoaluminum, increasing the electron density of aluminum. When the organoaluminum was coordinated with these additives, the active center of Zr was supposed to be reduced further, and the amount of the solid polymer by-product increased in the oligomerization of ethylene. The formation of a solid polymer by-product took place on the over-reduced Zr.

The amount of solid polymer by-product was also affected by various additives due to the difference in the electron density of the heteroatoms. These results are shown in Fig. 9. There was a good correlation of the electron density of the heteroatoms and the solid polymer quantity. Especially, when additives with an O atom such as furan and ether were added, the solid polymer formation remarkably increased.

4. Conclusions

A three-component catalyst of $ZrCl_4$ -TEA-EASC was found to be an industrially useful catalyst for

the oligomerization of ethylene. The catalyst was a slurry composed of a solid phase and a liquid phase; the active center of the catalyst was the Zr atom in the solid phase and the liquid phase. The solid polymer by-product seemed to be obtained on the over-reduced Zr. The catalytic activity was influenced by the method of preparation such as the addition order of the organoaluminum, temperature and time of aging. A highly active and stable catalyst was prepared when TEA was first added to the $ZrCl_4$ solution with successive addition of EASC and the mixture was heated above 70 °C for 30 min. It was proved from the NMR analysis that high activity was caused by the increase in the amount of TEA coordinated to $ZrCl_4$. The activity of the catalyst was increased by the coordination of the organoaluminum compound due to the reduction of Zr.

The coordination of additives such as THT and thiophene to Zr increase the electron density of Zr and suppress the insertion of the α -olefin into the Zr–Et bond due to steric hindrance. Therefore, the purity of the α -olefin was increased. On the other hand, additives with a high electron density of the heteroatom such as THF coordinated to the organoaluminum, as was confirmed by 2D-NMR COSY spectra. When TUF or ether compounds coordinated to Al atom as a ligand, the positive charge of Zr was considered to be significantly reduced.

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