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Nickel(II) Complex Bearing Fluorine-substituted α -Diimine Ligand Immobilized in Fluorotetrasilicic Mica Interlayer as Heterogeneous Catalysts for Ethylene OligomerizationHideki KUROKAWA^{†1)*}, Ryota OGAWA^{†1)}, Kazuhiro YAMAMOTO^{†2)}, Tsutomu SAKURAGI^{†2)},
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Heterogeneous α -diiminickel(II) catalysts were prepared by the direct reaction between nickel(II) ion-exchanged fluorotetrasilicic mica and the ligand [Ph'-N=C(Me)-C(Me)=N-Ph'; Ph' = C₆H₅-, 2-FC₆H₄-, 4-FC₆H₄-, 2,4-F₂C₆H₃-, and 2,4,6-F₃C₆H₂-]. When the prepared procatalysts were activated by a conventional alkyl aluminum compound, such as triethylaluminum or triisobutylaluminum, the high activity for ethylene oligomerization was readily obtained with the formation of linear α -olefins. The activity of the catalysts increased with the addition of fluorine atoms on the phenyl groups in the ligand, and the maximum activity (420 g-C₂ g-cat⁻¹ h⁻¹ at 0.7 MPa and 50 °C) was obtained by the catalysts containing 2,4-difluorophenyl groups, because fluorine atoms decreased the electron density of the nickel center. The oligomers were formed in good accordance with the Schulz-Flory distribution, and the values of the distribution constant were within 0.53–0.65. The selectivities of the linear α -olefins were not less than 90 mol% in all the runs. During all the oligomerization runs, long induction periods were clearly observed, but the period was shortened when the reaction temperature was raised. It seemed that the characteristic catalytic behavior was due to a complicated activation mechanism derived from the specific layered structure of the procatalysts.

KeywordsLayered clay mineral, α -Diiminickel complex, Clay mineral support, Ligand intercalation, Alkyl aluminum co-catalyst**1. Introduction**

Considerable attention has been paid to the development of new catalysts for the production of linear α -olefins based on late transition-metal complexes having a neutral ligand, because these complexes showed a high catalytic activity for both the polymerization and oligomerization of ethylene^{1)–5)}. As a first important report, nickel(II) complexes bearing a sterically less-hindered α -diimine ligand catalyzed the oligomerization of ethylene to form α -olefins when the complex was used in the presence of methylaluminoxane (MAO)^{6),7)}. These catalysts showed a high catalytic activity and selectivity to linear olefins under mild reaction conditions.

The electronic and steric effects on both the catalytic activity and the selectivity of linear α -olefins were systematically investigated by Helldörfer *et al.* using the

nickel complexes bearing a halogen-substituted α -diimine ligand; the nickel complexes bearing an *o*-, *m*-, or *p*-fluorine-substituted α -diimine ligand showed a moderate catalytic activity and only oligomers were formed in all the complexes^{8)–11)}. Apart from the α -diiminickel(II) complexes, a large number of nickel(II) complexes consisting of neutral ligands, such as diimine, iminopyridine, bis(imino)pyridine, iminoquinoline, bipyridine, and phenanthroline derivatives, have been developed^{12)–52)}; most of these complexes selectively afforded light olefins such as butenes and hexenes.

Recently, we developed iron and nickel complexes immobilized in clay mineral interlayers, and these catalysts acted as useful heterogeneous catalysts for ethylene polymerization by their activation with conventional alkyl aluminum compounds^{53)–56)}. These catalysts are readily prepared by the direct reaction of a metal ion-exchanged clay mineral and an appropriate ligand in a solvent. Moreover, the production of ethylene oligomers using these heterogeneous catalysts was easily achieved by modification of the ligand structure in the

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Fig. 1 Proposed Feature of α -Diiminonickel Complex Immobilized in Fluorotetrasilic Mica Interlayer

nickel-based catalysts⁵⁶). However, the modification significantly decreased the catalytic activity, and a considerable amount of undesirable polyethylene wax having a low melting temperature was still formed with the oligomers as a critical problem of these catalysts after the ligand modification.

Based on these results, it is necessary to improve the catalyst performances, and the aim of this study is to increase the catalytic activity of the nickel-based catalysts by applying the fluorine-modified α -diimine ligand to the immobilized nickel-based catalysts.

2. Experimental

Toluene, *n*-hexane, and other solvents were obtained from Kanto Chemical Co., Inc., and were dehydrated by MS-13x dried at 400 °C. They were degassed by N₂ bubbling and then stored under an inert gas atmosphere. The chemicals used for the ligand preparation were purchased from Tokyo Chemical Industry Co., Ltd. Fluorotetrasilic mica was supplied from COOP Chemical Co., Ltd. The precatalysts were handled by a standard Schlenk technique under a N₂ atmosphere. The precatalysts used in this study are summarized in Fig. 1.

2.1. Ligand Synthesis

The ligands L1-5 were prepared according to the method described in the literature with a slight modification^{8),9),56}. The typical procedure of the ligand synthesis is indicated below. Methanol (6 mL), 2,3-butanedione (0.287 g, 3.33 mmol), 2,4-difluoroaniline

(1.089 g, 8.42 mmol), and a few drops of glacial acetic acid were successively added to a N₂-purged 100-mL flask. The reaction was performed at ambient temperature for 96 h with stirring. The target ligand gradually precipitated with time. After the reaction, the crude ligand was washed with a small amount of dehydrated methanol. The pure ligand was obtained by drying the washed one at ambient temperature under reduced pressure. Instrumental analyses by ¹H-NMR (Bruker Avance III, resonance frequency for ¹H = 300 MHz) and double-focused sector MS (JEOL, AM 500, direct inlet and EI method) were used for the identification of the prepared ligands. The data of the prepared ligands L2-5 are displayed below.

L2:

Yield = 14 %

¹H-NMR: δ 2.18 (6H, s, -N=C-Me), δ 6.85-6.91 (4H, m, Ph), δ 7.08-7.13 (6H, m, Ph); MS (DI) *m/e* = 272 (parent ion), 136 (2-FPh-N=C⁺Me), 95 (FPh⁺).

L3:

Yield = 38 %

¹H-NMR: δ 2.15 (6H, s, -N=C-Me), δ 6.73-6.78 (2H, dd, 6-H-Ph), δ 7.07 (2H, dd, 5-H-Ph); MS (DI) *m/e* = 272 (parent ion), 136 (4-FPh-N=C⁺Me), 95 (FPh⁺).

L4:

Yield = 33 %

¹H-NMR: δ 2.16 (6H, s, -N=C-Me), δ 6.81-6.92 (6H, m, Ph); MS (DI) *m/e* = 308 (parent ion), 154 (2,4-F₂Ph-N=C⁺Me), 95 (F₂Ph⁺).

Table 1 Physicochemical Properties of Ni²⁺-mica^{a)}

Clay mineral	Composition [wt%]									Amount of Ni ²⁺ b)	Exchange [%]	BET SA ^{c)}
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	S	K ₂ O	CaO	Fe ₂ O ₃	NiO			
Na ⁺ -mica	6.4	31.1	0.6	59.3	-	-	-	< 0.1	-	-	-	3.3
Ni ²⁺ -mica	1.9	31.2	0.4	58.0	-	-	< 0.1	< 0.1	6.0	0.805	95 ^{d)}	3.9

a) The amount of fluorine was fixed at the constant value (2.48 wt%) described in the supplier specification, because fluorine was not detectable by this technique.

b) Amount of exchanged Ni²⁺ ions = $\mu\text{mol g}^{-1}$. ^{c)} BET surface area = $\text{m}^2 \text{g}^{-1}$.

d) Determined by the following equation.

$$M_{\text{Ni}}/[0.5(M_{\text{Na}}^{\text{b}} - M_{\text{Na}}^{\text{a}}) + 1.5(M_{\text{Al}}^{\text{b}} - M_{\text{Al}}^{\text{a}})]$$

M_{Ni} = mole of Ni²⁺ ions (amount of Ni²⁺ ions). M_{Na}^{b} and M_{Al}^{b} = moles of Na⁺ and Al³⁺ ions before ion-exchange reaction.

M_{Na}^{a} and M_{Al}^{a} = moles of Na⁺ and Al³⁺ ions after ion-exchange reaction.

L5:

Yield = 12 %

¹H-NMR: δ 2.20 (6H, s, -N=C-Me), δ 6.74-6.80 (4H, d, Ph); MS (DI) m/e = 344 (parent ion), 172 (2,4,6-F₃Ph-N=C⁺Me), 145 (2,4,6-F₃Ph-N⁺), 131 (F₃Ph⁺).

2. 2. Procatalyst Preparation

Nickel ion-exchanged fluorotetrasilicic mica (Ni²⁺-mica) was prepared according to a previous paper⁵⁵⁾. The physicochemical properties of the prepared Ni²⁺-mica are summarized in **Table 1**. To a 20-mL Schlenk flask, the prepared Ni²⁺/mica (0.25 g) and the acetonitrile solution of the appropriate ligand (850 mmol-ligand for 1 g Ni²⁺-mica) were added under a nitrogen atmosphere, and then allowed to react at 70 °C for 120 h. After the reaction, the solid part settled out and then the clear solution was carefully removed by a syringe. Acetonitrile, toluene, and *n*-hexane were used for successively washing the solid part. The procatalysts **L1-6**/Ni²⁺-mica were obtained by drying the solid at ambient temperature for 4 h under reduced pressure.

2. 3. Ethylene Oligomerization

An autoclave (120-mL volume) equipped with a magnetic stirrer, a pressure gauge, and valves to introduce the solvent, procatalyst, co-catalyst, and ethylene was used for the ethylene oligomerization. Solvent (including exactly weighed 0.1-mL *n*-tridecane as an internal standard), the procatalysts, and an activator (TEA or TIBA) were successively added to the autoclave, and the oligomerization reaction was performed at 40-80 °C and 0.7 MPa with a continuous supply of ethylene. After the oligomerization, 1.0 mL of a gas sample was extracted from the gas-phase in the autoclave and analyzed by a thermal conductivity detector (TCD) gas chromatograph to determine the amount of C₄ products in the gas-phase. The liquid phase was cooled to 0 °C in an ice bath and then the produced oligomers (C₆-C₂₂) were quantitatively determined by a gas chromatograph equipped with an hydrogen-flame ionization detector (FID) and a capillary column (methyl silicone, 0.25-mm internal diameter, 60 m). The ethylene consumption rate during the oligomerization

was measured using a mass-flow meter connected to the ethylene supply line. The activities in all the runs were determined by the total amount of the ethylene consumption.

2. 4. Characterization of Procatalyst

The compositions of Na⁺- and Ni²⁺-mica were determined by X-ray fluorescence (XRF) analysis (PANalytical B.V., PW2400). A mixture of the mica and cellulose (total = 0.250 g, oil shale : cellulose = 1 : 1 by weight) was molded into a wafer having a 10-mm diameter as a specimen for the XRF analysis.

The procatalyst and a small amount of dry liquid-paraffin were mixed under an inert gas atmosphere, and the obtained paste was placed on a glass specimen holder. The holder was covered with a polyester film to avoid exposure to air. The X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima III Spectrometer (operating conditions; X-ray = CuK α line (λ = 0.15406 nm), scan rate = 1.0 deg. min⁻¹, scan angle (2θ) = 3-15 deg., sampling step = 0.02 deg., voltage and current = 40 kV and 40 mA). The basal spacing of the procatalyst was determined from the (001) diffraction peak.

Thermogravimetry (TG) and a differential thermal analysis (DTA) were performed using a Shimadzu DTG-60 thermal analyzer. The procatalyst (5-7 mg) was weighed in a platinum sample pan in a glove box under a nitrogen atmosphere, and then placed in the TG-DTA apparatus. The operating conditions are as follows: heating rate = 10 °C min⁻¹, temperature range = r.t. to 700 °C, under a dry air atmosphere (50 mL min⁻¹).

3. Results and Discussion

3. 1. Ethylene Oligomerization Using L1-5/Ni²⁺-mica Procatalysts

The results of the ethylene oligomerization using the heterogeneous catalysts (procatalysts, **L1-5**/Ni²⁺-mica) based on α -diimine nickel complexes bearing the **L1-5** ligands are summarized in **Table 2**. The results of the ethylene oligomerization using the procatalyst **L1**/Ni²⁺-mica have already been reported in a previous paper⁵⁵⁾. The procatalysts (**L2-4**/Ni²⁺-mica) based on the com-

Table 2 Ethylene Oligomerization Using Heterogeneous Catalysts Prepared from F-substituted α -Diimine Ligand and Ni^{2+} -mica

Run	L	Activator	Activity [g-C ₂ g-cat ⁻¹ h ⁻¹]	Product ^{b)} [wt%]		S_{α} ^{c)} [%]	α ^{d)}	T_m ^{e)} [°C]
				Solid	C ₄ -C ₂₂			
1	1	TEA	73	4.1	58.6	96.4	0.59	NA
2	2	TEA	248	3.9	59.0	97.6	0.56	93, 109, 125
3	2	TIBA	208	4.9	63.6	96.5	0.57	91, 105, 125
4	3	TEA	170	8.1	53.5	97.6	0.65	91, 107, 125
5	3	TIBA	133	2.9	58.5	95.7	0.57	107, 126
6	4	TEA	347	6.5	70.0	97.0	0.55	89, 108, 125
7	4	TIBA	256	7.7	70.3	94.1	0.58	89, 108, 125
8	5	TEA	18	6.9	71.1	~100	0.53	NA
9	5	TIBA	26	7.3	102	~100	0.55	91, 107, 123

a) Reaction conditions; temperature = 60 °C, ethylene pressure = 0.7 MPa (gauge), activator = 1.02 mmol, cat. weight = 4.0 mg, solvent = *n*-heptane (50 mL).

b) "Solid" indicates the amount of the solid part recovered by filtration of the reaction mixture. "C₄-C₂₂" represents the amount of hydrocarbons having the carbon number 4-22.

c) Selectivity to α -olefins (average value of each selectivity calculated for C₁₀-C₁₈ products).

d) α (probability of chain propagation) = (moles of C_{*n*+2})/(moles of C_{*n*}). α was indicated as the average values of these calculated for *n* = 6-16.

e) Melting point of solid product. Italic values indicate shoulder peak. NA = not analyzed.

plexes bearing the α -diimine ligands containing phenyl groups substituted by mono- or di-fluorine atoms showed a much higher activity for the ethylene oligomerization compared to the procatalyst (**L1**/ Ni^{2+} -mica) based on the complex bearing no fluorine-substituted ligand **L1**. In contrast, an extremely low activity was observed during the ethylene oligomerization using the **L5**/ Ni^{2+} -mica procatalyst having the ligand containing 2,4,6-trifluorophenyl groups. The low activity of **L5**/ Ni^{2+} -mica can be explained by the following speculation. The electron withdrawing groups such as fluorine-substituted phenyl groups increase the positive net charge of the nickel center. Although the catalytic activity increases with increasing its positive charge, the nickel center having the excess positive-charge interacts strongly with ethylene, and the strong interaction prevents the insertion of ethylene into the metal-alkyl bond of the active species.

The highest activity was obtained by the **L4**/ Ni^{2+} -mica procatalysts having 2,4-difluorophenyl groups. Although the **L2-4**/ Ni^{2+} -mica procatalysts were readily activated by a conventional alkylaluminum compound, the activities of the procatalysts combined with TEA (Runs 2, 4, and 6) was slightly higher than those combined with TIBA (Runs 3, 5, and 7). The activation of the procatalyst by TEA was more readily than that by TIBA due to the higher Lewis acidity of TEA.

The synthesis of the nickel complex bearing a mono fluorine-substituted ligand (*o*-, *m*-, or *p*-fluorophenyl group on the nitrogen atoms) and its use for the homogeneous ethylene oligomerization combined with MAO were investigated by Helldörfer *et al.*⁹⁾ They reported that the nickel complex having *p*-fluorophenyl groups showed a much higher activity than those of other complexes. Moreover, they also reported that the oligomerization using the complexes bearing the ligand

Reaction conditions are the same as listed in Table 2.

Fig. 2 Distribution of Oligomers Obtained Using **L1-5**/ Ni^{2+} -mica Procatalysts in the Presence of TEA

containing the fluorophenyl group resulted in the formation of only ethylene oligomers, and the polyethylene (solid product) amount was not more than 1 wt% at 60 °C under 10 bar (1 bar = 1×10^5 Pa). The Schulz-Flory constants α obtained in all the runs were within 0.65-0.68. The α value is defined as the formula $R_p/(R_p + R_t)$, where R_p and R_t are the rates of the propagation and the chain transfer reaction, respectively.

On the contrary, the **L2-4**/ Ni^{2+} -mica catalysts afforded 2.9-8.1 wt% of polyethylene in addition to ethylene oligomers, and the α value (0.55-0.65) were slightly lower than those obtained by the homogeneous catalysts. The oligomer distributions are shown in **Fig. 2**. In all the runs, the oligomer distributions were in agreement with the Schultz-Flory equation, but considerable amounts of polyethylene (**Table 2**, "Solid") were produced. The results suggested that the active sites for

the polyethylene formation were different from those for the oligomer formation, because the amount of the formed polyethylene was much higher than that (not more than 0.1 wt%) estimated based on the obtained α value (0.7) and the assumed molecular weight of the polyethylene ($M_n > 1000 \text{ g mol}^{-1}$).

Figure 3 indicates the profiles of the ethylene consumption during the oligomerization using the **L1-5**/ Ni^{2+} -mica. In the initial stage of the oligomerization, the ethylene consumption was occasionally observed, which was caused by the ethylene absorption into the solvent. When **L1**/ Ni^{2+} -mica procatalyst was used for the oligomerization, the induction period was observed for approximately 30 min, but the period was shortened to within 20 min by replacing **L1** with the fluorine-containing **L2-4** ligand. Additionally, the maximum rate of ethylene consumption dramatically increased and the highest rate was obtained using the procatalyst

Reaction conditions are the same as listed in Table 2.

Fig. 3 Profiles of Ethylene Consumption during Ethylene oligomerization Using **L1-5**/ Ni^{2+} -mica Procatalysts in the Presence of TEA

consisting of the Ni^{2+} -mica and the **L4** ligand having 2,4-difluorophenyl groups.

3. 2. Ethylene Oligomerization Using **L4**/ Ni^{2+} -mica Procatalyst

Table 3 indicates the results of the ethylene oligomerization at 40–70 °C using the most active **L4**/ Ni^{2+} -mica procatalyst in the presence of R_3Al . The activity obtained by the catalysts combined with the **L4**/ Ni^{2+} -mica and TEA was similar to that obtained by the catalysts combined with **L4**/ Ni^{2+} -mica and TIBA. The total ethylene consumption increased when the temperature was raised from 40 to 50–60 °C, however, at 70 °C, the consumption clearly decreased due to the decomposition of the active species.

The higher reaction temperature favored the formation of the C_4 – C_{22} oligomers with the decreasing solid product, because the chain-transfer reaction was relatively promoted with the increasing temperature compared to the propagation reaction. The α values also decreased from 0.65 to 0.51 in the oligomerization using TEA and from 0.63 to 0.50 in those using TIBA with the increasing temperature. Meanwhile, the selectivity to α -olefins (S_α) gradually decreased with the increasing temperature, and this decrease was caused by the copolymerization between the produced α -olefins and ethylene. Moreover, it is well-known that the polymerization of ethylene using α -diimine nickel complexes affords a branch polyethylene by “chain walking,” which increased with the increasing reaction temperature⁵⁷. The increase in the “chain walking” resulted in the increasing mole fraction of branch oligomers.

Figure 4 indicates the oligomer distribution obtained using the **L4**/ Ni^{2+} -mica procatalyst combined with TEA. At the higher reaction temperature, the amount of C_4 and C_6 oligomers increased, however, on the contrary, the amount of C_{12} – C_{22} oligomers clearly decreased. The chain transfer reaction is dominant at the higher

Table 3 Ethylene Oligomerization Using **L4**/ Ni^{2+} -mica Procatalyst

Run	T_p [°C]	Activator	Activity [g- C_2 g-cat $^{-1}$ h $^{-1}$]	Product ^{b)} [wt%]		S_α ^{c)} [%]	α ^{d)}	T_m ^{e)} [°C]
				Solid	C_4 – C_{22}			
10	40	TEA	274	21.0	49.9	99.5	0.65	104, 127
11	50	TEA	302	14.9	60.7	97.1	0.63	90, 107, 128
6	60	TEA	347	6.5	70.0	97.0	0.55	89, 108, 125
12	70	TEA	163	0.3	72.2	92.1	0.51	NA
13	40	TIBA	236	23.0	51.7	99.6	0.63	87, 107, 126
14	50	TIBA	420	14.6	60.7	95.0	0.62	86, 106, 125
7	60	TIBA	256	7.7	70.3	94.1	0.58	89, 108, 125
15	70	TIBA	192	0.7	80.4	91.8	0.50	NA

a) Reaction conditions; ethylene pressure = 0.7 MPa (gauge), activator = 1.02 mmol, cat. weight = 4.0 mg, solvent = *n*-heptane (50 mL).

b) “Solid” indicates the amount of the solid part recovered by filtration of the reaction mixture. “ C_4 – C_{22} ” represents the amount of hydrocarbons having the carbon number 4–22.

c) Selectivity to α -olefins (average value of each selectivity calculated for C_{10} – C_{18} products).

d) α (probability of chain propagation) = (moles of C_{n+2})/(moles of C_n). α was indicated as the average values of these calculated for n = 6–16.

e) Melting point of solid product. Italic values indicate shoulder peak. NA = not analyzed.

Reaction conditions are the same as listed in Table 3.

Fig. 4 Distribution of Products in Ethylene Oligomerization at 40–70 °C Using **L4**/ Ni^{2+} -mica Procatalyst in the Presence of TEA

Reaction conditions are the same as listed in Table 3.

Fig. 5 Profiles of Ethylene Consumption during Ethylene Oligomerization Using **L4**/ Ni^{2+} -mica Procatalyst in the Presence of TEA

reaction temperature compared with the chain propagation reaction. The change in the oligomer distribution was in good agreement with that of the α value.

Figure 5 indicates the ethylene consumption profiles during the oligomerization using the **L4**/ Ni^{2+} -mica in the presence of TEA. At 40 °C, a 15-min induction period was observed in the profiles and then the consumption rate gradually increased with the reaction time. After 1 h, the consumption rate reached a maximum, and then a slow deactivation was observed. When the temperature was raised from 40 to 50 °C, the induction period disappeared and the maximum consumption rate increased. The consumption rate obtained at 70 °C was much lower than that obtained at 60 °C, therefore, the highest value of the consumption

Reaction conditions are the same as listed in Table 3.

Fig. 6 Profiles of Ethylene Consumption during Ethylene Oligomerization Using **L4**/ Ni^{2+} -mica Procatalyst in the Presence of TIBA

rate was obtained at 60 °C. The low consumption rate at 70 °C is due to the deactivation of the catalyst, because the deactivation markedly occurred with the increasing reaction temperature.

The ethylene consumption profiles using the **L4**/ Ni^{2+} -mica in the presence of TIBA are summarized in **Fig. 6**. Although the activities (calculated on the basis of the total ethylene consumption) obtained using TIBA were nearly equal to those obtained using TEA, the consumption profiles were clearly different; a short induction period was observed even at 60 °C during the oligomerization using TIBA, and a longer time was needed until the rate attained a maximum. The important role of R_3Al is generally understood to be an alkylating agent of a metal complex in the homogeneous system, and the alkylation step is also required for the activation of the complex in this catalyst system. The reactivity of TIBA is considered to be much less than that of TEA, therefore, the low reactivity of TIBA is one of the reasons for the long activation time. Moreover, the characteristic structure of the clay mineral-based catalysts might affect the induction period. A high catalytic activity was readily obtained by the clay mineral-based catalysts when they were activated by R_3Al as well as MAO, suggesting that R_3Al took part in the formation of the active species by adsorption on the clay mineral surface. The relationship between the structure and the catalytic behavior of the procatalyst is discussed in Section 3.3.

3.3. Characterization of the Procatalyst by XRD Measurement

The XRD profiles of the prepared procatalysts, the dried Ni^{2+} -mica, and that treated with only CH_3CN are summarized in **Fig. 7**. The basal spacing of the dried Ni^{2+} -mica was 1.0 nm corresponding to the thickness of a mica sheet. When the dried Ni^{2+} -mica was treated

Spectra (a) and (b) indicate Ni^{2+} -mica after drying at 200 °C (a) and treating it with only CH_3CN (b), respectively. Spectra (c-g) correspond to the procatalysts prepared with Ni^{2+} -mica and **L1** (c), **L2** (d), **L3** (e), **L4** (f), and **L5** (g) in CH_3CN . The measurement of samples (b-g) was performed after drying at 110 °C.

Fig. 7 XRD Profiles of the Procatalysts and Related Materials

in CH_3CN , the distance between adjacent layers expanded to 1.21 nm, indicating that CH_3CN was intercalated into the mica interlayer. In all the procatalysts, expansion of the basal spacing was observed, but each value of the basal spacing was clearly different. The **L1** and **L3**/ Ni^{2+} -mica procatalysts showed a large expansion of the spacing, and these values were 1.54 nm and 1.47 nm, respectively. In contrast, the basal spacings of the **L2**, **L3**, and **L4**/ Ni^{2+} -mica procatalysts were relatively small at 1.32, 1.27, and 1.30 nm, respectively. The difference between the basal spacings was caused by the different conformations of the formed complexes on the inside of the interlayer. Moreover, the activity order of the procatalysts did not coincide with that of the distance between adjacent layers. For example, the **L4**/ Ni^{2+} -mica procatalyst showed the highest activity among the used procatalysts, but the basal spacing was relatively small. At this stage, we do not understand the reason for the difference in the basal spacing due to the lack of information about the structure of the formed complex, however, it seems that the basal spacing and the peak intensity were highly relevant to not only the amount of the formed complexes, but also the three-dimensional structure of the complex located in the interlayer.

Figure 8 indicates the profiles of the TG-DTA analysis for (b) Ni^{2+} -mica treated with only CH_3CN and (a) the procatalyst (**L4**/ Ni^{2+} -mica). In both profiles (a) and (b), the weight loss by the endothermic reaction was clearly observed around 40 °C, and that loss was 3.5–3.7 wt% of the total weight. This reaction could be attributed to the elimination of the physically adsorbed CH_3CN from the interlayer space. After the

Profiles (a) and (b) indicate Ni^{2+} -mica treated with only CH_3CN and the **L4**/ Ni^{2+} -mica procatalyst, respectively (sample weight: (a) 6.618 mg, (b) 4.743 mg).

Fig. 8 Thermal Analysis Results of the **L4**/ Ni^{2+} -mica Procatalyst

elimination of CH_3CN , the weight loss continued in both (a) and (b). The weight loss of the profile (b) in the temperature range of 150–250 °C was due to the elimination of the CH_3CN coordinated to the metal ions, because no similar weight decrease was observed in the same temperature range in the TG profile of the Ni^{2+} -mica dried at 200 °C. Meanwhile, in profile (a), the exothermic reaction was clearly observed at 320 °C, indicating that the metal complex placed in the interlayer space had decomposed. The weight gradually decreased over 400 °C with small peaks due to the exothermic reactions (474 °C and 536 °C). The total weight loss in the temperature range of 150–700 °C was 8.4 wt% (0.558 mg), and this value corresponded to 187 mmol g-cat⁻¹ of the **L4**Ni(vacant)₂ complex (molar mass = 449 g mol⁻¹). The “vacant” term in the chemical formula means the vacant site of the complex, and now we consider that an oxygen atom of the mica sheets weakly coordinated to the Ni center through the vacant site. The amount of nickel(II) ions in the interlayer (805 mmol g-mica⁻¹) was determined by an XRF analysis, and 23 % of the nickel ions participated in the formation of the metal complexes. Based on both the thermal analysis results and the activity, the calculated turn-over frequency in Run 6 (**L4**/ Ni^{2+} -mica combined with TEA) was 18.4 s⁻¹.

Finally, we discuss the activation mechanism of the

procatalysts. From the value of the basal spacing, both ethylene and R_3Al were not able to access the complexes located deep inside the interlayer. Therefore, it was considered that the activation of the complex took place at the edge of the stacked lamellae, and the formed active sites produced oligomers and a small amount of polymer. The stacked lamellae were peeled off each other by the growth of the polymer chain, and then the inside complexes became accessible. This activation mechanism was assumed based on the ethylene polymerization using the catalysts consisting of the group IV metallocene complex and the cation exchanged-fluorotetrasilicic mica⁵⁸. The existence of the induction period and its temperature dependence can be consistently explained by this mechanism. A deeper understanding of detailed activation mechanism is currently in progress.

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References

- Bianchini, C., Giambastiani, G., Rios, I. G., Mantovani, G., Meli, A., Segarra, A. M., *Coord. Chem. Rev.*, **250**, 1391 (2006).
- Speiser, F., Braunstein, P., Saussine, L., *Acc. Chem. Res.*, **38**, 784 (2005).
- Bianchini, C., Giambastiani, G., Rios, I. G., Mantovani, G., Meli, A., Segarra, A. M., *Coord. Chem. Rev.*, **254**, 431 (2010).
- Wang, S., Sun, W.-H., Redshaw, C., *J. Organomet. Chem.*, in press. (dx. doi. org/10.1016/j.jorganchem.2013.08.021).
- Gao, R., Sun, W.-H., Redshaw, C., *Catal. Sci. Technol.*, **3**, 1172 (2013).
- Killian, C. M., Johnson, L. K., Brookhart, M., *Organometallics*, **16**, 2005 (1997).
- Svejda, S. A., Brookhart, M., *Organometallics*, **18**, 65 (1999).
- Helldörfer, M., Backhaus, J., Milius, W., Alt, H. G., *J. Mol. Catal. A: Chem.*, **193**, 59 (2003).
- Helldörfer, M., Backhaus, J., Milius, W., Alt, H. G., *J. Mol. Catal. A: Chem.*, **197**, 1 (2003).
- Helldörfer, M., Backhaus, J., Alt, H. G., *Inorg. Chim. Acta.*, **351**, 34 (2003).
- Helldörfer, M., Alt, H. G., *J. Appl. Polym. Sci.*, **89**, 1356 (2003).
- Schareina, T., Hillebrand, G., Fuhrmann, H., Kempe, R., *Eur. J. Inorg. Chem.*, 2421 (2001).
- Wang, L., Sun, W.-H., Han, L., Yang, H., Hu, Y., Jin, X., *J. Organomet. Chem.*, **658**, 62 (2002).
- Shao, C., Sun, W.-H., Li, Z., Hu, Y., Han, L., *Catal. Commun.*, **3**, 405 (2002).
- Spencer, L. P., Altwer, R., Wei, P., Gelmini, L., Gauld, J., Stephan, D. W., *Organometallics*, **22**, 3841 (2003).
- Jie, S., Zhang, D., Zhang, T., Sun, W.-H., Chen, J., Ren, Q., Liu, D., Zheng, G., Chen, W., *J. Organomet. Chem.*, **690**, 1739 (2005).
- Du, J., Li, L.-J., Li, Y., *Inorg. Chem. Commun.*, **8**, 246 (2005).
- Bluhm, M. E., Folli, C., Walter, O., Döring, M., *J. Mol. Catal. A: Chem.*, **229**, 177 (2005).
- Sun, W.-H., Zhang, S., Jie, S., Zhang, W., Li, Y., Ma, H., Chen, J., Wedeking, K., Fröhlich, R., *J. Organomet. Chem.*, **691**, 4196 (2006).
- Benito, J. M., de Jesús, E., de la Mata, F. J., Flores, J. C., Gómez, R., Gómez-Sal, P., *Organometallics*, **25**, 3876 (2006).
- Zhang, M., Zhang, S., Hao, P., Jie, S., Sun, W.-H., Li, P., Lu, X., *Eur. J. Inorg. Chem.*, 3816 (2007).
- Wang, L., Zhang, C., Wang, Z.-X., *Eur. J. Inorg. Chem.*, 2477 (2007).
- Irgang, T., Keller, S., Maisel, H., Kretschmer, W., Kempe, R., *Eur. J. Inorg. Chem.*, 4221 (2007).
- Jie, S., Zhang, S., Sun, W.-H., *Eur. J. Inorg. Chem.*, 5584 (2007).
- Adewuyi, S., Li, G., Zhang, S., Wang, W., Hao, P., Sun, W.-H., Tang, N., Yi, J., *J. Organomet. Chem.*, **692**, 3532 (2007).
- Song, Y., Zhang, S., Deng, Y., Jie, S., Li, L., Lu, X., Sun, W.-H., *Kinet. Catal.*, **48**, 664 (2007).
- Sun, W.-H., Wang, K., Wedeking, K., Zhang, D., Zhang, S., Cai, J., Li, Y., *Organometallics*, **26**, 4781 (2007).
- Gao, R., Zhang, M., Liang, T., Wang, F., Sun, W.-H., *Organometallics*, **27**, 5641 (2008).
- Xiao, L., Jie, S., Yingxia Song, Y., Cao, X., Sun, W.-H., *J. Organomet. Chem.*, **693**, 3858 (2008).
- Zhang, M., Gao, R., Hao, X., Sun, W.-H., *J. Organomet. Chem.*, **693**, 3867 (2008).
- Yang, Y., Yang, P., Zhang, C., Li, G., Yang, X.-J., Wu, B., Janiak, C., *J. Mol. Catal. A: Chem.*, **296**, 9 (2008).
- Armitage, A. P., Champouret, Y. D. M., Grigoli, H., Pelletier, J. D. A., Singh, K., Solan, G. A., *Eur. J. Inorg. Chem.*, 4597 (2008).
- Gao, R., Xiao, L., Hao, X., Sun, W.-H., Wang, F., *Dalton Trans.*, 5645 (2008).
- Chen, Y., Hao, P., Zuo, W., Gao, K., Sun, W.-H., *J. Organomet. Chem.*, **693**, 1829 (2008).
- Yang, P., Yang, Y., Zhang, C., Yang, X.-J., Hu, H.-M., Gao, Y., Wu, B., *Inorg. Chim. Acta*, **362**, 89 (2009).
- Li, J., Gao, T., Zhang, W., Sun, W.-H., *Inorg. Chim. Acta*, **362**, 166 (2009).
- Liu, F.-S., Gao, H.-Y., Song, K.-M., Zhang, L., Zhu, F.-M., Wu, Q., *Polyhedron*, **28**, 1386 (2009).
- Mukherjee, S., Patel, B. A., Bhaduri, S., *Organometallics*, **28**, 3074 (2009).
- Kyogoku, K., Yamada, C., Suzuki, Y., Nishiyama, S., Fukumoto, K., Yamamoto, H., Indo, S., Sano, M., Miyake, T., *J. Jpn. Petrol. Inst.*, **53**, (5), 308 (2010).
- Lee, G. M., Appukuttan, V. K., Suh, H., Ha, C.-S., Kim, I., *Catal. Lett.*, **141**, 1608 (2011).
- Chena, X., Zhanga, L., Yub, J., Haob, X., Liub, H., Sun, W.-H., *Inorg. Chim. Acta*, **370**, 156 (2011).
- Song, S., Xiao, T., Liang, T., Wang, F., Redshaw, C., Sun, W.-H., *Catal. Sci. Technol.*, **1**, 69 (2011).
- Song, S., Xiao, T., Wang, L., Redshaw, C., Wang, F., Sun, W.-H., *J. Organomet. Chem.*, **699**, 18 (2012).
- Lai, J., Hou, X., Liu, Y., Redshaw, C., Sun, W.-H., *J. Organomet. Chem.*, **702**, 52 (2012).
- Hou, X., Liang, T., Sun, W.-H., *J. Organomet. Chem.*, **708-709**, 98 (2012).
- Chandran, D., Lee, K. M., Chang, H. C., Song, G. Y., Lee, J.-E., Suh, H., Kim, I., *J. Organomet. Chem.*, **718**, 8 (2012).
- Chai, W., Yu, J., Wang, L., Hu, X., Redshaw, C., Sun, W.-H., *Inorg. Chim. Acta*, **385**, 21 (2012).
- Schweinfurth, D., Su, C.-Y., Wei, S.-C., Braunstein, P., Sarkar, B., *Dalton Trans.*, **41**, 12984 (2012).
- Chandran, D., Byeon, S. J., Suh, H., Kim, I., *Catal. Lett.*, **143**, 717 (2013).
- Hao, P., Song, S., Xiao, T., Li, Y., Redshaw, C., Sun, W.-H., *Polyhedron*, **52**, 1138 (2013).
- Ainooson, M. K., Guzei, I. A., Lara, C., Spencer, L. C., Darkwa, J., *Polyhedron*, **53**, 295 (2013).
- Rossetto, E., Caovilla, M., Thiele, D., de Souza, R. F., Bernardo-Gusmão, K., *Appl. Catal. A: General*, **454**, 152

- (2013).
- 53) Kurokawa, H., Matsuda, M., Fujii, K., Ishihama, Y., Sakuragi, T., Ohshima, M., Miura, H., *Chem. Lett.*, **36**, 1004 (2007).
- 54) Fujii, K., Ishihama, Y., Sakuragi, T., Ohshima, M., Kurokawa, H., Miura, H., *Catal. Commun.*, **10**, 183 (2008).
- 55) Kurokawa, H., Nakazato, Y., Tahara, S., Katakura, T., Ishihama, Y., Sakuragi, T., Miura, H., *Macromol. React. Eng.*, **7**, 125 (2013).
- 56) Kurokawa, H., Miura, K., Yamamoto, K., Sakuragi, T., Sugiyama, T., Ohshima, M., Miura, H., *Catalyst*, **3**, 125 (2013).
- 57) Johnson, L. K., Killian, C. M., Brookhart, M., *J. Am. Chem. Soc.*, **117**, 6414 (1995).
- 58) Kurokawa, H., Morita, S., Matsuda, M., Suzuki, H., Ohshima, M., Miura, H., *Appl. Catal. A: General*, **360**, 192 (2009).

要 旨

フッ素四ケイ素雲母層間に固定化されたフッ素原子置換 α -ジイミン配位子を有するニッケル (II) 錯体を不均一系触媒とするエチレンのオリゴメリゼーション

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ニッケル交換したフッ素四ケイ素雲母と配位子 [$\text{Ph}'\text{-N}=\text{C}(\text{Me})\text{-C}(\text{Me})=\text{N-Ph}'$; $\text{Ph}'=\text{C}_6\text{H}_5$ -, 2- FC_6H_4 -, 4- FC_6H_4 -, 2,4- $\text{F}_2\text{C}_6\text{H}_3$ -, および 2,4,6- $\text{F}_3\text{C}_6\text{H}_2$ -] の直接反応により不均一系 α -ジイミンニッケル触媒を調製した。調製した触媒を汎用のアルキルアルミニウム化合物であるトリエチルアルミニウムやトリイソブチルアルミニウムによって活性化すると、直鎖 α -オレフィン類を生成するエチレンのオリゴメリゼーションに対して高い触媒活性が容易に得られた。配位子のフェニル基上にフッ素原子を導入すると触媒活性が向上し、2,4-ジフルオロ

フェニル基を持つ触媒で最高活性が得られた。このフッ素原子の触媒活性への効果は、フッ素原子がニッケルの電子密度を低下させたためである。生成したオリゴマーの組成はシュルツ・フローリー分布に従い、その定数は0.53~0.65であった。直鎖 α -オレフィンへの選択率は、すべての実験で90 mol% 以上であった。すべての重合において明瞭な長い誘導期が観測され、それは反応温度を上昇させると短くなった。この興味深い触媒挙動は、触媒の特異な層状構造に由来する複雑な活性化メカニズムのためと考えられる。