

Article

Oligomerization of Ethylene to Produce Linear α -Olefins Using Heterogeneous Catalyst Prepared by Immobilization of α -Diiminonickel(II) Complex into Fluorotetrasilicic Mica Interlayer

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Abstract: Heterogeneous catalysts for production of linear α -olefins from ethylene were prepared by the direct reaction of the α -diimine ligand [L: R-N=C(R')-C(R')=N-R; R' = Me and R = 2,6-Me₂Ph (**L5**), 2,5-Me₂Ph (**L1**), 2-MePh (**L2**), or Ph (**L3**); R' = 1,8-naphth-diyl and R = Ph (**L4**)] and Ni²⁺ ion-exchanged fluorotetrasilicic mica. Only high molecular weight polyethylene was obtained in the reaction using the **L5**/Ni²⁺-Mica procatalyst activated by AlEt₃ (TEA) as an activator, whereas the TEA-activated **L1**- and **L2**/Ni²⁺-Mica procatalysts afforded a mixture of a large amount of low-molecular weight polyethylene and a small amount of oligomers having 4-22 carbons. The procatalyst consisting of Ni²⁺-Mica and the **L3** ligand that possesses non-substituted phenyl groups on the iminonitrogen atoms effectively promoted the oligomerization of ethylene after its activation with TEA, resulting in the fact that the ethylene oligomers were produced with a moderate catalytic activity (101 g-ethylene g-cat⁻¹ h⁻¹ at 0.7 MPa-ethylene) in the presence of TEA. When the backbone was varied from the butane moiety (**L3**) to acenaphthene (**L4**), the solid product dramatically increased. The weight percentage of the oligomers in the total products

increased with the increasing reaction temperature; however, an insignificant increase in the oligomers was observed when the ethylene pressure was decreased.

Keywords: polymerization; polyethylene; clay minerals; intercalation

1. Introduction

α -Olefins (terminal alkenes) of carbon number 4–20 are important basic products in the chemical industry, and these are used as the comonomer in the ethylene/ α -olefin copolymerization, the raw material of long-chain alcohols, and the base material of synthetic lubricant oil [1,2]. Straight chain olefins produced by the oligomerization of ethylene are more useful than branched olefins, because of the high biodegradability of the products. The one-step process using a triethylaluminum catalyst was developed by the Gulf Oil Chemical Co. (Chevron Corp.) to produce ethylene oligomers having the Shultz-Flory distribution [1]. The two-step process using the same catalyst is known as the Ethyl process (Albemarle Corp.) and the products have a Poisson distribution with a relatively narrow distribution [1]. These processes required both a high reaction temperature and ethylene pressure due to the low catalytic activity of triethylaluminum [1].

The sophisticated ethylene-oligomerization process was developed by Shell and called the Shell Higher Olefin Process (SHOP) [1–3]. In the SHOP, the ethylene oligomerization catalyzed by nickel complexes affords ethylene oligomers having a Shultz-Flory distribution, and the composition of the oligomers is adjusted to the required composition through the reaction combined with both isomerization of the olefins and disproportionation between the light and heavy olefins [3]. Idemitsu Kosan Co., Ltd., developed a new ethylene oligomerization process based on the catalyst consisting of $ZrCl_4$, an alkylaluminum compound, and a Lewis base; this excellent process is able to control the product distribution by changing the ligand structure [3,4].

In the last decade of the 20th century, attractive catalysts, such as the α -diiminenickel complexes and bis(imino)pyridineiron complexes, were successively discovered by Brookhart *et al.* and Gibson *et al.* These complexes combined with MAO act as highly active catalysts for the oligomerization of ethylene to produce linear α -olefins [5–8]. Subsequently, many researchers have investigated various catalysts based on the nickel, cobalt, and iron complexes [9–13].

Recently, we developed new heterogeneous catalysts, which were prepared through the intercalation of the ligand into the late transition-metal ion exchanged clay mineral, and the coordination of the bis(imino)pyridine or α -diimine ligand to the interlayer metal ion; these catalysts showed a high activity for the polymerization of ethylene in the presence of not only MAO, but also alkyl aluminum compounds [14,15]. Moreover, the steric and/or electronic properties of these heterogeneous catalysts can be changed by modification of the ligand structures, which are used in the homogeneous catalysts. As an example of the ligand modification, an iron complex bearing the acetylaminopyridine ligand instead of the bis(imino)pyridine ligand, which was immobilized into the mica interlayer, effectively produced linear α -olefins with a high activity [16].

In the present study, we attempted to develop heterogeneous ethylene oligomerization catalysts to produce α -olefins by decreasing the steric bulk around the nickel center in α -diiminenickel(II) complex

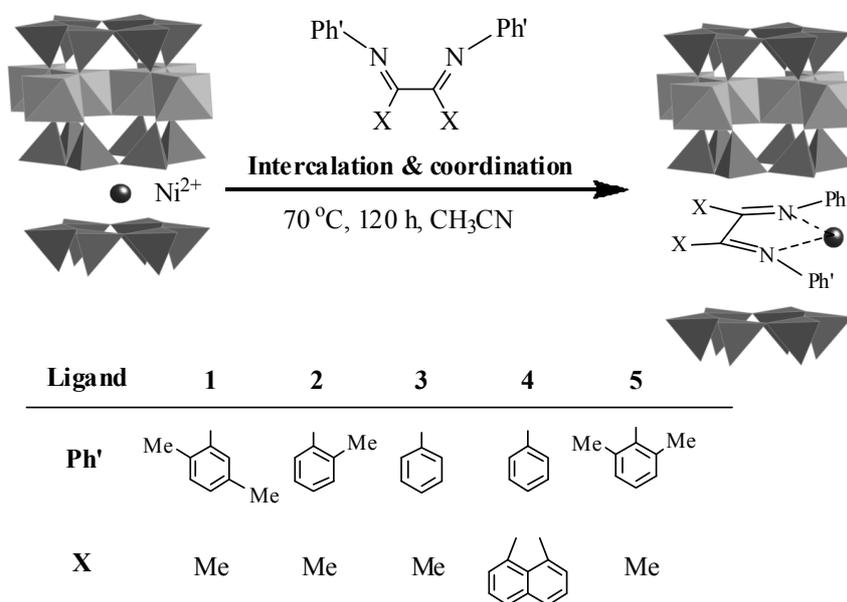
immobilized in a fluorotetrasilicic mica interlayer. Helldörfer *et al.* reported that the α -diiminonickel(II) complex, having a less hindered ligand, acts as a catalyst for ethylene oligomerization when the complex was combined with MAO [17,18].

2. Results and Discussion

2.1. Oligomerization of Ethylene Using **L1–4**/ Ni^{2+} -Mica Procatalysts

The outline of the prepared procatalysts is displayed in Figure 1. Our previous report indicated that the procatalyst prepared from the Ni^{2+} -Mica and the ligand **L5** having 2,6-dimethylphenyl groups on the iminonitrogen atoms [$\text{Ph}'\text{-N}=\text{C}(\text{Me})\text{-C}(\text{Me})=\text{N-Ph}'$, $\text{Ph}' = 2,6\text{-Me}_2\text{Ph}$] afforded both a high catalytic activity and high molecular-weight polyethylene that included methyl branches formed by the “chain walking” mechanism [15]. Many researchers reported that the molecular weight of the polyethylene decreased with the decreasing steric hindrance around the metal center of the rate transition-metal polymerization catalysts [7], and therefore, we attempted the oligomerization of ethylene using the procatalysts prepared from the Ni^{2+} -Mica and ligands **L1–4**; these ligands were expected to afford a less-hindered environment around the metal center in the formed complex than the **L5**. The relationship between the ligand structure and the catalyst performance (the catalytic activity, the amount of solid and liquid products, and the selectivity to α -olefins = S_α) are summarized in Table 1.

Figure 1. Proposed feature of α -diiminonickel complex immobilized in fluorotetrasilicic mica interlayer.



The procatalyst prepared using ligand **L1** that has the 2,5-dimethylphenyl groups on the iminonitrogens was a magnitude less active than the reference procatalyst prepared with ligand **L5**. Although the surprising difference between the activities obtained by the two procatalysts is not fully understood, the activity (= total ethylene consumption) of this procatalyst was often dominated by the amount of the complex formed in the interlayer. The structure of the α -diiminonickel complex, which shows an activity for the ethylene polymerization/oligomerization, has a distorted tetrahedral

geometry, and the ratio of the ligand to the nickel ion is 1 (LNiX₂, L: bidentate α -diimine ligand, X: halogen). Meanwhile, the coordination of the two bidentate iminopyridine ligands to one nickel ion (L₂NiX₂) affords a complex with the distorted octahedral geometry, and this octahedral complex shows no significant activity for the ethylene polymerization compared to the tetrahedral one [19]. It is considered that **L1** more readily formed the L₂Ni²⁺-type complex than **L5**, and as a result, the amount of the LNi²⁺-type complex dramatically decreased when the less-hindered ligand **L1** was used.

Table 1. Oligomerization of ethylene using heterogeneous α -diiminonickel(II) catalysts ¹.

Run	L	Time /h	Activity /g-C ₂ g-cat ⁻¹ h ⁻¹	Product/wt% ²		S _a ³ /%	T _m ⁴ /°C
				Solid	C ₄ -C ₂₂		
1	1	1.5	193	94.9	4.4	72.1	128
2	2	1.5	188	87.9	6.2	74.4	127
3	3	2.0	101	22.1	53.9	91.2	125
4	4	1.5	96	71.7	12.6	92.5	128
Ref. [15]	5	1.0	1804	100	0	-	120

¹ Reaction conditions; temperature = 50 °C, ethylene pressure = 0.7 MPa (gauge), activator = TEA (1.02 mmol), cat. weight = 4.0 mg, solvent = *n*-heptane (50 mL). ² “Solid” indicates the amount of solid part recovered by filtration of reaction mixture. “C₄-C₂₂” represents the amount of hydrocarbons having carbon numbers 4–22.

³ Selectivity to α -olefins (average value of each selectivity calculated for C₁₀-C₁₈ products). ⁴ Melting point of solid product.

The activities of the procatalyst prepared from the butane-backbone ligands **L1–3** gradually decreased with the decreasing number of methyl substituents on the iminophenyl group (Runs 1–3). The difference between the activities of the **L1**/Ni²⁺-Mica and the **L3** analogy was much lower than that between the **L1**/Ni²⁺-Mica and the **L5** analogy, indicating that the removal of one methyl substituent at the *O*-position strongly affected the formation of the L₂NiX₂-type complex. Therefore, the trend in the activity observed among the **L1–3**/Ni²⁺-Mica procatalysts is due to electronic effects rather than steric effects.

The substituent located at the *o*-position also affected the products. In our catalyst system, when one methyl group was removed from the *o*-position on both iminophenyl groups, the product changed from a high molecular-weight polyethylene ($M_n = 10^6$ g mol⁻¹, Run ref.) to a low molecular-weight one ($M_n = 0.91 \times 10^4$ g mol⁻¹, Run 3). Upon removing the two methyl substituents from both *O*-positions on the iminophenyl groups, the chain length dramatically shortened and the amount of the liquid products increased.

Figure 2 shows the distribution of the oligomers obtained using the **L1–4**/Ni²⁺-Mica procatalysts. The product distribution was in good agreement with the Shultz-Flory distribution. No significant difference was observed among the distributions obtained by the four procatalysts, though the weight ratios of the oligomers to the solid part were significantly different. Moreover, a larger amount of the solid product was formed when compared to the amount expected from the distribution. These facts suggested that most of the solid product was formed on the active-site that differed from the site producing the oligomers. Helldörfer *et al.* reported that only 1-butene was formed by the ethylene oligomerization using the homogeneous catalyst consisting of the **L3**-NiBr₂ complex and MAO [17].

The products obtained by the **L3/Ni²⁺**-Mica catalyst were quite different from those obtained by the corresponding homogeneous catalyst. Clear evidence of this characteristic difference is not obtained at this stage; however, the nature of the active center might be affected by the strong electrostatic interaction between the cation complex and the mica sheet having negative charges.

Figure 2. Distribution of products from ethylene oligomerization using **L1–4/Ni²⁺**-Mica procatalyst. Reaction conditions are the same as in Table 1.

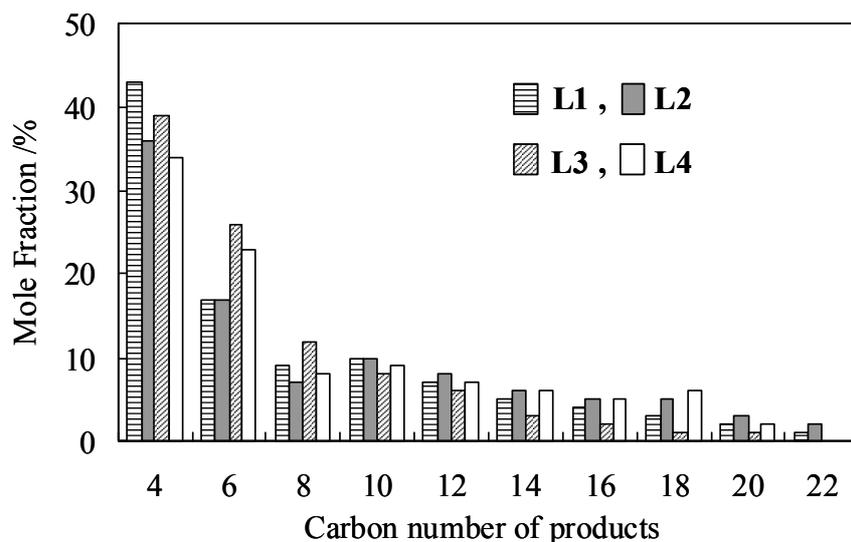
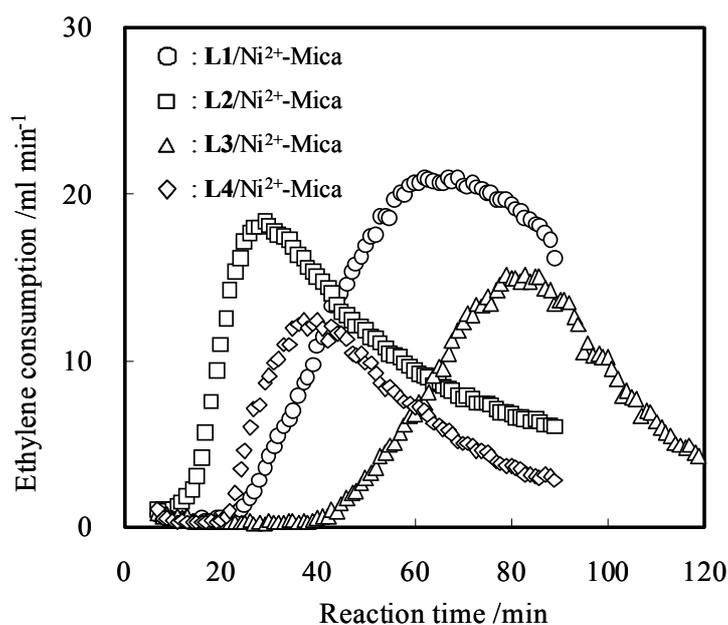


Figure 3. Profiles of ethylene consumption from ethylene oligomerization using **L1-4/Ni²⁺**-Mica procatalyst. Reaction conditions are the same as in Table 1.



The time dependence of the ethylene consumption during the oligomerization is shown in Figure 3. In all the consumption profiles, the induction period was clearly observed. After this period, the consumption gradually increased, reached a maximum, then rapidly decreased due to deactivation of the active species. The intervals of the induction period observed during the oligomerization using **L1–4**/Ni²⁺-Mica were different between each of them, but no clear correlation between the ligand structures was observed.

2.2. Detailed Evaluation of **L3**/Ni²⁺-Mica Procatalysts

The effects of the reaction temperature and ethylene pressure on the productivity of the oligomers were investigated using the **L3**/Ni²⁺-Mica procatalyst. These results are summarized in Table 2. When the temperature was raised from 50 °C to higher temperatures (Runs 3, 5, and 6), the productivity dramatically decreased with the increasing weight ratio of the C₄–C₂₂ products to total products. This increasing ratio of the oligomers is due to the relative increase in the rate of the chain transfer reaction to the rate of the propagation, and this trend is in good agreement with the trends observed for the ethylene polymerization using other polymerization catalysts.

Table 2. The results of ethylene oligomerization using **L3**/Ni²⁺-Mica under various reaction conditions ¹.

Run	T_0 ²	P ³	Time /h	Productivity /g-C ₂ g-cat ⁻¹ h ⁻¹	Product/wt% ⁴		S_a ⁵	T_m ⁶
	/°C	/bar			Solid	C ₄ –C ₂₂	/%	/°C
3	50	0.7	2.0	101	22.1	53.9	91.2	124.5
5	60	0.7	1.5	67	15.3	61.2	88.2	122.0
6	70	0.7	1.5	14	6.9	71.1	78.8	-
7	50	1.0	1.5	165	25.3	54.5	93.8	124.5
8	50	0.4	1.5	88	19.2	53.1	88.1	123.0
9 ⁷	60	0.7	2.0	71	9.2	83.5	87.8	123.1

¹ Reaction conditions; activator = TEA (1.02 mmol), cat. weight = 4.0 mg, solvent = *n*-heptane (50 mL).

² Oligomerization temperature. ³ Ethylene pressure. ⁴ “Solid” indicates the amount of solid part recovered by filtration of reaction mixture. “C₄–C₂₂” represents the amount of hydrocarbons having carbon numbers 4–22. ⁵ Selectivity to α -olefins (average value of each selectivity calculated for C₁₀–C₁₈ products). ⁶ Melting point of solid product. ⁷ Activator = TIBA (1.02 mmol).

The decreasing ethylene pressure decreased the productivity because of the decrease in the monomer concentration, which was expected from the standard polymerization mechanism (Runs 3, 7, and 8). Meanwhile, the ratios of the oligomers to total products were constant within 53–55%, suggesting that the transfer reaction of the β -hydrogen of the polymer chain to ethylene mainly took place on the active site. In a previous study, the molecular weight of the obtained PE clearly decreased with the decreasing ethylene pressure during the polymerization using **L5**/Ni²⁺-Mica [15]. This interesting difference in the catalytic behavior between the **L3** and **L5**/Ni²⁺-Mica procatalysts might be due to the difference in the steric hindrance around the metal center. In the procatalyst **L3**/Ni²⁺-Mica, the steric hindrance around the active site was lower than that of **L5**/Ni²⁺-Mica, therefore, ethylene readily approached the metal center with the bulky polymer chain, resulting in the transfer reaction of

β -hydrogen to ethylene predominantly occurring. When TIBA was used as an activator (Run 9), the productivity was nearly equal to that obtained by the oligomerization using TEA. The increasing amount of the oligomers was observed in Run 9: however, this was due to the increasing amount of the C_4 products, which were caused by the TIBA decomposition to produce isobutane.

The effect of the temperature on the distribution of the C_4 – C_{22} oligomers is displayed in Figure 4. The products were formed in accordance with the Shultz-Flory distribution in the tested temperature range, and no significant difference was observed among the distributions.

Figure 4. Distribution of products from ethylene oligomerization at 50–70 °C using $L3/Ni^{2+}$ -Mica procatalyst. Reaction conditions are the same as in Table 1.

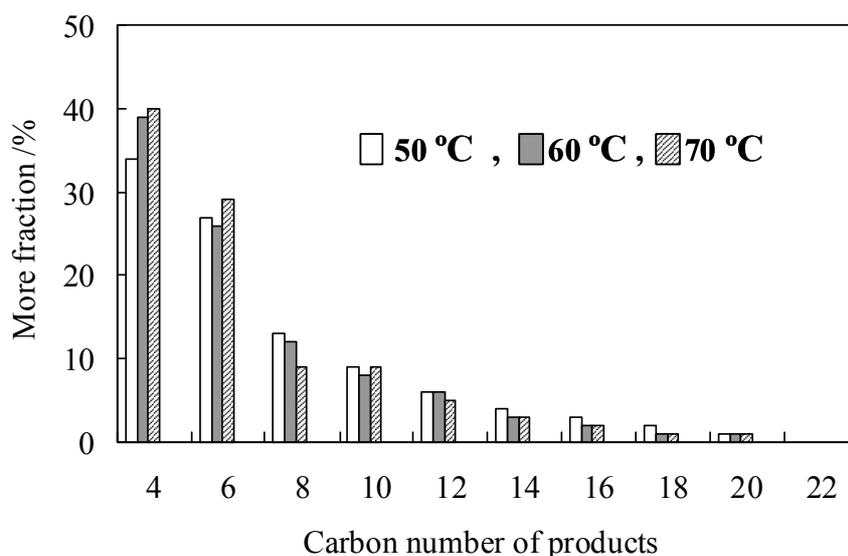


Figure 5. Profiles of ethylene consumption from ethylene oligomerization at 50–70 °C using $L3/Ni^{2+}$ -Mica procatalyst. Reaction conditions are the same as in Table 1.

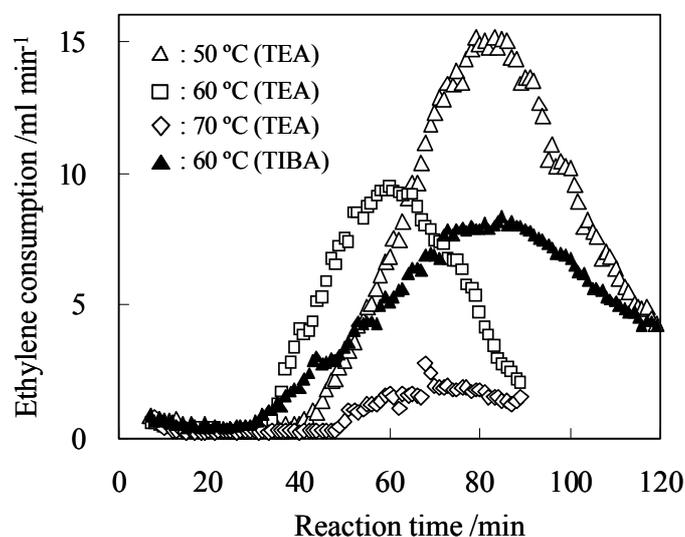
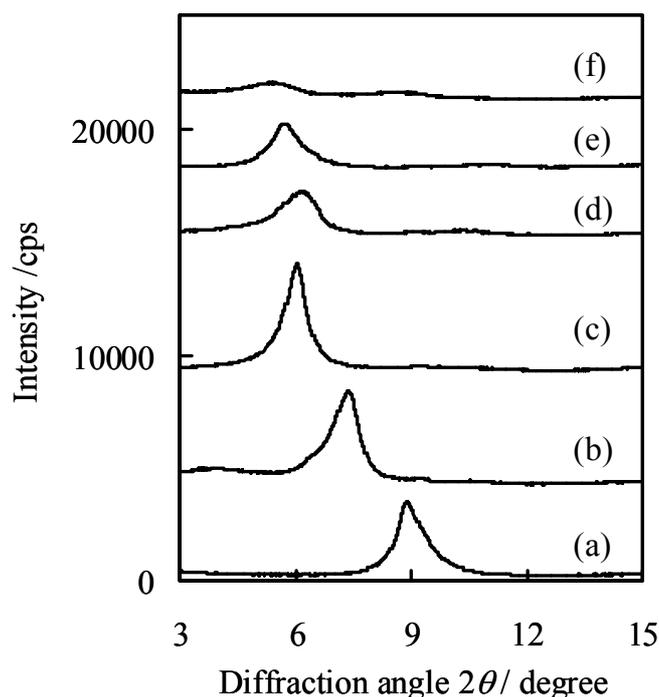


Figure 5 shows the trends in the ethylene consumption during the oligomerization. When the temperature was raised from 50 to 60 °C, the induction period was shortened and the peak rate of the ethylene consumption clearly decreased. At 70 °C, the rate of the consumption was extremely lower than that observed above 50 °C. These facts strongly indicated that the active species were unstable above 50 °C. When the activator TEA was replaced with TIBA, the profile of the ethylene consumption was obviously changed; the induction period was lengthened and the deactivation after the peak of the consumption rate was slower than that observed in the oligomerization using TEA. This difference was due to the weaker reactivity of TIBA than that of TEA.

2.3. Characterization of Procatalysts

The characterization of the procatalysts was performed using XRD and the obtained patterns are summarized in Figure 6. The basal spacing of the Ni²⁺-exchanged mica after the calcinations was 1.00 nm (Figure 6a).

Figure 6. XRD patterns of the procatalysts and related materials. Ni²⁺-Mica after drying at 200 °C (a) and treated with only CH₃CN (b); L1 (c); L2 (d); L3 (e), and L4 (f) in CH₃CN. The measurement of samples (b)–(f) were performed after drying at 110 °C.



When Ni²⁺-Mica was treated with only CH₃CN (solvent), the basal spacing was expanded to 1.21 nm, indicating that the CH₃CN was introduced into the interlayer space, and the monolayer of CH₃CN was formed (Figure 6 (b)). The profiles of the procatalysts L1–4/Ni²⁺-Mica are also displayed in Figure 6 (c–f). In the profile (c) obtained for the L1/Ni²⁺-Mica, the peak corresponding to the basal spacing expanded to 1.47 nm without any decreasing peak intensity. The intercalation of the ligand L1 into the mica interlayer and its coordination to the Ni²⁺ center caused the expansion of the basal spacing. In the profiles (d, e) obtained from the L2 and L3/Ni²⁺-Mica, expansion of the basal spacing

was also observed (1.43 nm for (d) and 1.54 nm for (e)), but the peak intensities decreased along with broadening of the peak. The very weak and broad peak derived from the basal spacing was observed in the XRD profile (f) obtained from the **L4**/ Ni^{2+} -Mica due to the irregularity of the stacking sheets. The ligands **L1-3** having the butane moiety are highly flexible; therefore, the electrostatic interaction between the adjacent sheets and the complex changes the ligand structure to the thermodynamically favorable one, whereas the mica sheets are irregularly stacked in the **L4**/ Ni^{2+} -Mica procatalyst, because **L4** is a relatively rigid structure compared to **L1-3**, and the change in the structure hardly occurred in the interlayer space.

3. Experimental Section

The chemicals used for the ligand and procatalyst preparation were obtained from Kanto Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd. Fluorotetrasilicic mica was obtained from COOP Chemical Co., Ltd. The chemicals used for the preparation of the procatalysts were dehydrated by MS-13X dried at 400 °C. The preparation and handling of the procatalysts were performed by a standard Schlenk technique under a N_2 atmosphere.

3.1. Ligand Synthesis

The ligands **L1-3** were prepared by the reaction of 2,3-butanedione and the corresponding aniline in the same manner reported in the literature [17]. The **L2** synthesis is described below as a typical preparation procedure. Into a N_2 -purged 100 mL flask, MS-13X (4.0 g), 40 mL of dehydrated toluene, 0.323 g (3.75 mmol) of 2,3-butanedione, 1.017 g (10.9 mmol) of aniline, and the catalyst ($\text{SiO}_2\text{-Al}_2\text{O}_3$, 0.5 g) were successively added. The reaction was performed at 40 °C for 24 h. After the reaction, the catalyst and MS-13X were filtered from the mixture, and the solvent was removed under reduced pressure. The solid product was purified by recrystallization in alcohol (MeOH:EtOH = 3:1).

The **L4** ligand having an acenaphthene backbone was prepared by the condensation reaction of acenaphthenequinone and aniline. Fifty milliliters of toluene, 0.822 g (4.51 mmol) of acenaphthenequinone, 1.071 g (11.5 mmol) of aniline, and 6 mg of *p*-toluenesulfonic acid were successively added into the N_2 -purged 100 mL flask. The mixture was then allowed to react at 130 °C for 24 h. The resulting solution was passed through a short SiO_2 column and then the crude product was obtained by removing the solvent. The product was purified by recrystallization in toluene.

The prepared ligands were identified using $^1\text{H-NMR}$ (Bruker Avance III, resonance frequency for $^1\text{H} = 300$ and 500 MHz) and double-focused sector MS (JEOL, AM 500, direct inlet and EI method). The results of the ligand synthesis are summarized below.

L1: Yield = 32%. $^1\text{H-NMR}$: δ 2.07 (6H, s, 2-Me-Ph), δ 2.11 (6H, s, -N=C-Me), δ 2.32 (6H, s, 5-Me-Ph), δ 6.65 (2H, s, 6-H-Ph), δ 6.85 (2H, d, 4-H-Ph), δ 7.2 (2H, d, 3-H-Ph); MS (DI) $m/e = 292$ (parent ion), 146 (2,5-Me₂Ph-N=C⁺(Me)).

L2: Yield = 11%. $^1\text{H-NMR}$: δ 2.1 (12H, s, -N=C-Me and Ph-Me), δ 6.65 (2H, d, 6-H-Ph), δ 7.03 (2H, t, 5-H-Ph), δ 7.2 (4H, m, 3- and 4-H-Ph); MS (DI) $m/e = 264$ (parent ion), 249 (**L3** -Me).

L3: Yield = 30%. $^1\text{H-NMR}$: δ 2.15 (6H, s, -N=C-Me), δ 6.8 (4H, d, 2- and 6-H-Ph), δ 7.1 (2H, t, 4-H-Ph), δ 7.4 (4H, dd, 3- and 5-H-Ph); MS (DI) $m/e = 236$ (parent ion), 118 (Ph-N=C⁺(Me)).

L4: Yield = 60%. $^1\text{H-NMR}$: δ 6.83 (2H, d, H-AN), δ 7.13 (4H, d, 2- and 6-H-Ph), δ 7.25-7.35 (2H, m, H-AN), δ 7.38 (2H, t, 4-H-Ph), δ 7.48 (4H, t, 3- and 5-H-Ph), δ 7.9 (2H, d, H-AN); MS (DI) m/e = 332 (parent ion), 255 (**L4-Ph**).

3.2. Procatalyst Preparation

The nickel ion-exchanged fluorotetrasilicic mica (Ni^{2+} -Mica) was prepared by a method reported in a previous paper [20]. The dried Ni^{2+} /Mica 0.25 g was weighed into a 20-mL Schlenk flask under a nitrogen atmosphere, and then the acetonitrile solution of the appropriate ligand (850 μmol -ligand for 1 g Ni^{2+} -Mica) was added. The obtained suspension was treated at 70 °C for 120 h in order to prepare the α -diiminenickel complex in the fluorotetrasilicic mica interlayer. After the treatment, the solution was carefully removed using a syringe, and then the solid was successively washed with acetonitrile, toluene, and *n*-hexane. The resulting product was finally dried at ambient temperature for 4 h under reduced pressure to obtain the **L1-4**/ Ni^{2+} -Mica procatalysts.

3.3. Characterization of Procatalyst

The procatalyst was mixed with a small amount of dry liquid paraffin under an inert gas. The paste was placed on a glass specimen holder and then covered with a polyester film to avoid exposure to air. The prepared specimen was characterized by an X-ray diffraction measurement using a Rigaku Ultima III Spectrometer (operating conditions; X-ray = $\text{CuK}\alpha$ line ($\lambda = 0.15406$ nm), scan rate (2θ) = $1.0^\circ \text{ min}^{-1}$, scan angle (2θ) = $3\text{--}15^\circ$, sampling step = 0.02° , voltage and current = 40 kV and 40 mA). The basal spacing of the procatalyst was determined by the (001) diffraction peak.

3.4. Ethylene Oligomerization

Fifty milliliter of *n*-heptane including the exactly weighed *n*-tridecane (0.5 mL, internal standard) was added to a 120-mL autoclave equipped with a magnetic stirrer, a pressure gauge, and a valve in order to introduce the ethylene. After adding the triethylaluminum (TEA) solution and the slurry of the procatalyst into the autoclave, it was placed in a water bath maintained at 40–50 °C. The oligomerization was performed for 1–2 h by monitoring the ethylene consumption. After the reaction, the internal gas was purged to a gas sampling bag in order to analyze the butanes in the gas phase using a TCD gas chromatograph (Porapak Q, 2 m), and then the autoclave was cooled to nearly 0 °C in an ice bath. The butenes and ethylene oligomers having carbon numbers from 6 to 22 ($\text{C}_6\text{--C}_{22}$) were analyzed using an FID gas chromatograph (dimethylpolysiloxane, 0.25 mm-i.d., 60 m). After the solid product (polyethylene) was recovered by filtration, that was analyzed using DSC to determine the melting point. The activity was calculated based on the total ethylene consumption, and the amount of each product (solid and $\text{C}_4\text{--C}_{22}$) was indicated as the percentage by weight of the total ethylene consumption. The distribution of the $\text{C}_4\text{--C}_{22}$ products was normalized to a mole percentage.

4. Conclusions

The heterogeneous catalysts used for ethylene oligomerization were successfully developed by the direct reaction of the α -diimine ligand and Ni^{2+} ion-exchanged fluorotetrasilicic mica. The product

dramatically changed from a high molecular weight polyethylene to polyethylene wax and soluble oligomers when the methyl substituent was removed from the phenyl group on the iminonitrogen atom. The moderate yield of the oligomers and high selectivity to the linear α -olefins was achieved using the procatalyst consisting of the [Ph-N=C(CH₃)-C(CH₃)=N-Ph] ligand and Ni²⁺-exchanged fluorotetrasilicic mica.

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Conflict of Interest

The authors declare no conflict of interest.

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