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Acetyliminopyridineiron(III) Complexes Immobilized in Fluorotetrasilicic Mica Interlayer as Efficient Catalysts for Oligomerization of Ethylene

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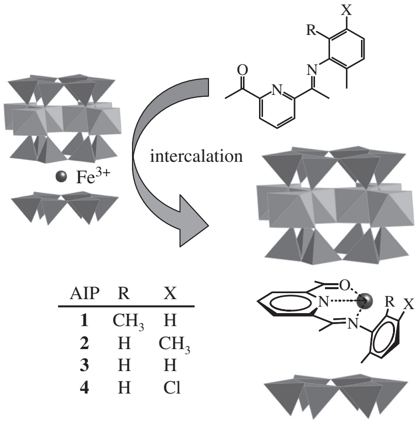
As new heterogeneous catalysts, the 2-acetyl-6-{1-[(2,3,6-trisubstituted phenyl)imino]ethyl}pyridineiron(III) complexes immobilized in the fluorotetrasilicic mica interlayers were prepared by the reaction of acetyliminopyridine and Fe^{3+}-exchanged fluorotetrasilicic mica. The catalysts showed a high activity for the ethylene oligomerization with a high selectivity to linear α-olefins in the presence of R'_3Al ($R' =$ Et and *i*-Bu) as an activator.

The shell higher olefin process (SHOP) based on Ni(II) complexes is the well-known process to produce ethylene oligomers that are used as the raw materials of detergents, lubricants, and various fine chemicals in addition to their use as comonomers in ethylene polymerization.[1] In 1998, two research groups independently discovered that catalysts consisting of a bis(imino)pyridineiron(II) complex and methylaluminoxane (MAO) exhibited an extremely high activity for ethylene oligomerization and a high selectivity for the formation of linear α-olefins.[2] In recent decades, the design and synthesis of new late-transition-metal complexes have attracted considerable attention by researchers.[3] To use these catalysts in practical applications, immobilization of the metal complex on an inorganic carrier is desirable, and we previously reported that the heterogeneous catalysts prepared by the immobilization of bis(imino)pyridineiron(III)[4] and α-diiminenickel(II)[5] complexes in the fluorotetrasilicic mica interlayer showed a high activity for the ethylene polymerization. In this study, we attempted to immobilize the acetyliminopyridineiron(III) complexes in a fluorotetrasilicic mica interlayer with the aim of developing useful heterogeneous catalysts for ethylene oligomerization to produce α-olefins.

Detailed procedures for the synthesis of acetyliminopyridines (AIP) **1**–**4** and Fe^{3+}-changed fluorotetrasilicic mica (Fe^{3+}-Mica, 482 µmol-Fe^{3+} per 1 g) are described in the Supporting Information.[6] The dried Fe^{3+}-Mica was allowed to react with the ligand (200 µmol for 1 g of Fe^{3+}-Mica) in acetonitrile at 70 °C for 120 h. The precatalyst was obtained by washing the solid part with the solvent (CH_3CN, toluene, and hexane) and subsequently drying at ambient temperature for 4 h under reduced pressure. The prepared precatalysts are outlined in Figure 1.

Ethylene was oligomerized in heptane at 50–70 °C and 0.4 MPa ethylene pressure for 1–2 h using the precatalyst in the presence of triethylaluminum (TEA), triisobutylaluminum (TIBA), or MAO. The activity was determined by the total amount of the consumed ethylene. The formed oligomers having carbon numbers 4–20 (C_4–C_{20}) were analyzed by FID-GC (GC-14A Shimadzu, DB-1 capillary column, 0.25 mm i.d. × 60 m). The precatalysts were characterized by XRD analysis (Ultima-RINT, Rigaku Corporation) and FT-IR measurement (Jasco FT/IR 4100).



AIP	R	X
1	CH_3	H
2	H	CH_3
3	H	H
4	H	Cl

Figure 1. Outline of precatalysts.

The results of the ethylene oligomerization are listed in Table 1. The precatalyst **1** consisting of AIP **1** having the 2,6-dimethylphenyl group on an imino nitrogen atom produced polyethylene (PE, $M_n = 34700$, PDI $= 9.0$) with a high catalytic activity (Entry 1). On the contrary, the precatalyst **2** prepared by the reaction of Fe^{3+}-Mica and AIP **2** (2,5-dimethylphenyl group on an imino nitrogen atom) exhibited an extremely high activity for the ethylene oligomerization and afforded the linear α-olefins along with a small amount of low-molecular-weight PE ($M_n < 1500$, Entry 3). The steric bulk around the metal center in the precatalyst **2** was lower than that in the precatalyst **1**, resulting in the chain-transfer reaction occurring more frequently on the precatalyst **2** than on the precatalyst **1**. Moreover, the activity of the precatalyst **2** was higher than that of the precatalyst **1**, because of the high accessibility of ethylene to the active center in the precatalyst **2**. The base material Fe^{3+}-Mica (without ligand treatment) was completely inactive for the ethylene polymerization/oligomerization under the same reaction conditions in the presence of R'_3Al.

The activity based on the total amount of the ethylene consumption increased with the increasing reaction temperature up to 60 °C, indicating that the active species were stable at 60 °C (Entries 2 and 3). When the temperature was raised to 70 °C, the total amount of the ethylene consumption slightly decreased (Entry 4) due to the faster deactivation of the active species. The precatalyst **2** exhibited a high selectivity for linear α-olefins (>95%), and the oligomer distribution[6] follows the Schulz–Flory distribution, which can be characterized by the constant α. The precatalysts that have a 2-methylphenyl group (precatalyst **3**) and a 2-methyl-5-chlorophenyl group (precatalyst **4**) also showed an activity for the ethylene oligomerization, but the activity obtained by precatalysts **3** and **4** were approximately one-third of that obtained by precatalyst **2**. Although the α value

Table 1. Results of ethylene oligomerization using immobilized iron(III) complexes[a]

Entry	Precatalyst	T^b/°C	Activator	Activity[c]	Product/wt %		Mass balance[d]	Selectivity[e] /wt %	α^f
					C_4–C_{20}	Solid			
1	**1**	60	TIBA	450	0	100	113	—	—
2	**2**	50	TIBA	3750	83.8	8.4	92.2	96.7	0.57
3	**2**	60	TIBA	7800	84.5	11.3	95.8	97.4	0.61
4	**2**	70	TIBA	6480	88.4	9.9	98.3	98.1	0.56
5	**2**	60	TEA	3750	87.6	6.9	94.5	96.7	0.55
6	**2**	60	MAO	7010	87.2	10.0	97.2	96.9	0.52
7[g]	**3**	60	TIBA	1970	76.5	13.5	90.0	96.2	0.57
8[g]	**4**	60	TIBA	2700	65.9	18.4	84.3	97.1	0.61
9[h]	Fe^{3+}-Mica	60	TIBA	0	—	—	—	—	—
10[i]	**2**–$FeCl_3$	60	MAO	7170[j]	93.1	2.3	95.4	98.9	0.51
11[i]	**2**–$FeCl_3$	60	TIBA	0	—	—	—	—	—

[a]Reaction conditions: precatalyst (1.0 mg, 200 µmol-ligand/g-Fe^{3+}-Mica), activator (0.40 mmol), heptane (50 mL), time (1 h), ethylene pressure (0.4 MPa, gauge). [b]Reaction temperature. [c]Total amount of ethylene consumption determined by a mass flow meter. Activity: g-ethylene g-cat^{-1} h^{-1}. [d]Mass balance: 100 × (total amount of products)/(total amount of ethylene consumption). [e]Selectivity to linear α-olefins calculated based on the C_{10}–C_{16} products. [f]Schulz–Flory constant α (average of α_8–α_{14}), $\alpha_n = C_{n+2}\,(\text{mol})/C_n\,(\text{mol})$. [g]Reaction time: 2 h. [h]Fe^{3+}-Mica (without ligand treatment) was used for the oligomerization as a precatalyst. [i]Reaction conditions; **2**-$FeCl_3$: 0.2 µmol, Al/Fe = 2000, solvent: toluene (50 mL). [j]Activity: kg-ethylene mol-Fe^{-1} h^{-1}.

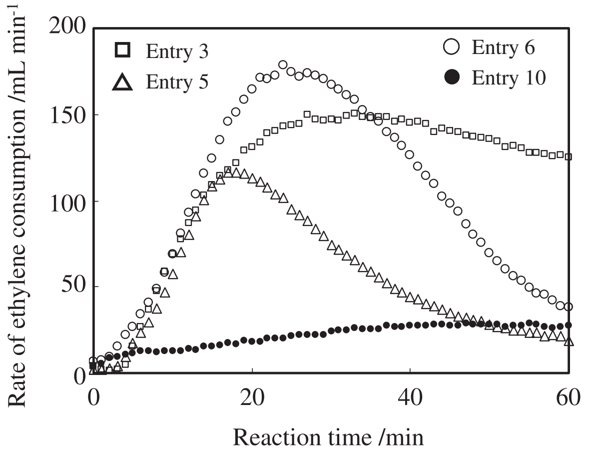


Figure 2. Profiles of ethylene consumption using heterogeneous (precatalyst **2**/R'_3Al) and homogeneous (**2**–$FeCl_3$/MAO) catalysts.

obtained by precatalyst **4** was nearly equal to the values obtained by the other precatalysts, a large amount of solid products was formed. The solid products might be formed on a site different from that of the oligomers formation. Nickel- and cobalt-based acetyliminopyridine complexes were often used for the ethylene oligomerization, but the report of the oligomerization using the AIP iron complex was rare. An attractive example using the AIP complex having a *m*-3-(trifluoromethyl)phenyl group on the imino nitrogen atom was only reported by Bluhm et al., and the α values obtained using that complex were 0.36–0.39.[7]

Figure 2 shows the profiles of the ethylene consumption during the oligomerization using precatalyst **2** (Entries 3, 5, and 6) in addition to the profile obtained by the homogeneous catalyst (Entry 10). When the **2**–$FeCl_3$/MAO catalyst was used for the oligomerization, the activity was lower than those obtained by the precatalyst **2**. Moreover, the catalyst consisting of **2**–$FeCl_3$/TIBA did not show any significant activity during the oligomerization. When precatalyst **2** was used as the catalyst in the presence of R'_3Al, the ethylene consumption gradually increased, and the high r_{max} values were observed 20–30 min after supplying the ethylene. These facts indicated that the active species in our catalysts was effectively formed and have a long lifetime, especially when TIBA was used as the activator. The highest r_{max} was obtained using precatalyst **2** with MAO, but remarkable deactivation was observed. The value of α obtained by the oligomerization with MAO was slightly lower than those obtained by the oligomerization with R'_3Al.

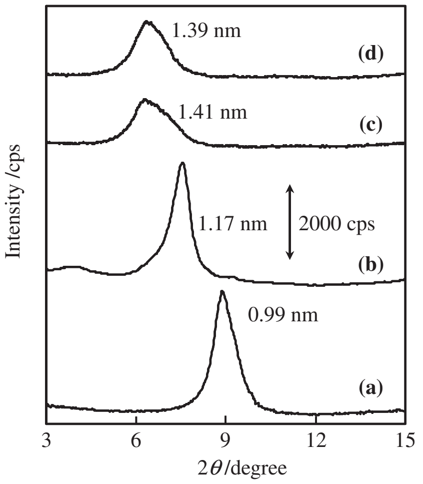


Figure 3. XRD profiles of (a) Fe^{3+}-Mica (dried at 200 °C under reduced pressure), (b) Fe^{3+}-Mica (treated only with CH_3CN), (c) precatalyst **1**, and (d) precatalyst **2**. The profiles of samples (b)–(d) were measured after drying at 110 °C under reduced pressure.

The prepared precatalysts were characterized by XRD analysis (Figure 3) and FT-IR spectra (Figure 4).

When Fe^{3+}-Mica was treated with the ligand in CH_3CN, the basal spacing determined by the XRD measurement increased

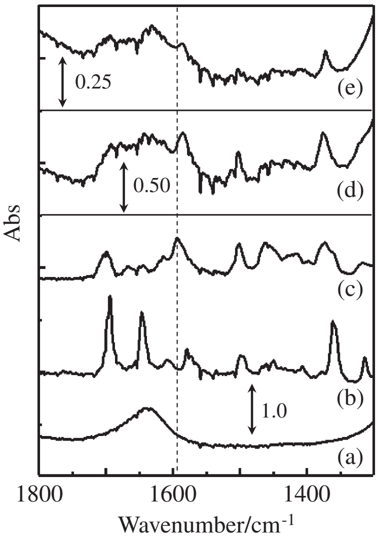


Figure 4. IR spectra of (a) Fe^{3+}-Mica, (b) AIP **2**, (c) **2**-$FeCl_3$ complex, (d) precatalyst **2** (560 μmol-**2**/g-Fe^{3+}-Mica), and (e) precatalyst **2** (200 μmol-**2**/g-Fe^{3+}-Mica).

from 0.99 to 1.41 nm for precatalyst **1** and 1.39 nm for precatalyst **2**, indicating that the interlayer space expanded with the intercalation of the ligand.[8] In the FT-IR measurement of the precatalyst **2**, the characteristic absorption band derived from the coordinated C=N bond was observed at 1586 cm^{-1}, strongly supporting the fact that the complex was effectively formed in the interlayer space of the mica.

Finally, based on FT-IR measurements using standard samples prepared with **2**–$FeCl_3$ and mica,[6] the amount of the formed complexes in the precatalyst **2** was determined as 111 μmol g-$mica^{-1}$, indicating that 55% of the used ligand contributed to the formation of the complexes. The TON value ($7.0 \times 10^2 s^{-1}$) in Entry 3 (precatalyst **2**) was calculated based on the amount of the formed complex and the total amount of the ethylene consumption. The activity of the precatalyst **2**/TIBA was much higher than that of homogeneous **2**–$FeCl_3$/MAO catalyst, because the TON value in Entry 10 (**2**–$FeCl_3$/MAO catalyst) was 71 s^{-1}.

In conclusion, the heterogeneous catalysts prepared by the immobilizing acetyliminopyridineiron(III) complex in the fluorotetrasilicic mica interlayer have characteristics, such as a high catalytic activity, easy activation with conventional alkyl aluminum, and a long lifetime of the active species, moreover, the catalyst and products were readily separated by filtration.

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8 The XRD profiles were measured with Cu Kα radiation (wavelength: 0.15406 nm) at the scan rate of 1.0 degree min^{-1}.