Catalytic Behavior of Bis(imino)pyridineiron(II) Complex Supported on Clay Minerals during Slurry Polymerization of Ethylene

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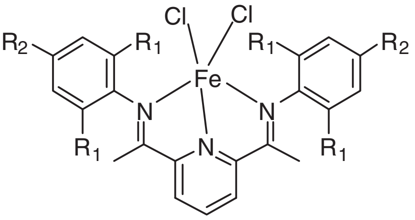
Supported catalysts prepared by an impregnation method using the bis(imino)pyridineiron(II) complex and clay minerals (montmorillonite, fluorotetrasilicic mica, and saponite) were used for ethylene polymerization. The activities of the montmorillonite- and saponite-based catalysts were much higher than that of the mica-based one.

A bis(imino)pyridineiron(II) complex activated with methylalumoxane (MAO) catalyzes the polymerization of ethylene with high activity and affords characteristic polyethylene with a broad molecular-weight distribution.[1–3] The discovery of these catalysts has stimulated research interests, resulting in a large number of iron complexes being synthesized and tested for the polymerization of α-olefins.[4,5] These highly active catalysts based on Fe complexes require MAO as activators. Moreover, when a conventional alkylaluminum, such as triethylaluminum (TEA) and triisobutylaluminum (TIBA), was used as the activator instead of MAO, the activity was much lower than that using MAO.

Montmorillonite, a typical layered clay mineral, is able to activate metallocene complexes in the presence of conventional alkylaluminum, and the resulting catalysts show high activity for α-olefin polymerization.[6–9] The success of clay mineral-based catalysts afforded a significant interest in view of the mechanistic study of the formation of the active species in addition to their advantages for practical use.

In this study, we attempted the development of supported catalysts consisting of bis(imino)pyridineiron(II) complex and clay mineral supports on the premise that TIBA was mainly employed for the polymerization to avoid homogeneous polymerization with the soluble active species produced by the reaction of MAO and the supported iron(II) complexes.



1: $R_1 = R_2 = CH_3$-
2: $R_1 = (CH_3)_2CH$-, $R_2 = H$

Figure 1. Structures of bis(imino)pyridineiron(II) complexes.

Experimental

The bis(imino)pyridineiron(II) complexes (Figure 1) with different structures were prepared according to the literature.[2] Fluorotetrasilicic mica (Mica), montmorillonite (Mont), and saponite (Sapo) were used as the clay minerals (Mica was purchased from CO-OP Chemical Co., Ltd. Sapo and Mont were purchased from the Clay Science Society of Japan). The ion-exchanged layered clay minerals were prepared by the ion-exchange reaction of Na^+ clay minerals in an aqueous solution of metal nitrate. After the reaction, the solid part was calcined at 200 °C for 4 h and then dried at the same temperature for 4 h under reduced pressure. The dried support was treated with a dichloromethane solution containing the bis(imino)pyridineiron(II) complex ($1.0\,\mu mol\,mL^{-1}$) at ambient temperature for 30 min under a nitrogen atmosphere. After the solvent was removed, the solid part was dried for 1 h under reduced pressure to obtain the procatalyst. The amount of the Fe complex on the support was adjusted to $50\,\mu mol$ g-support^{-1}. The ethylene was polymerized at 40–60 °C and 0.2–0.7 MPa for 1 h using a 120 mL autoclave equipped with a magnetic stirrer. The number-average molecular weight (M_n) and polydispersity index (PDI) of the produced polyethylene were determined by GPC.

Results and Discussion

Ethylene polymerization was performed using a **1**/M^{n+}–Mica procatalyst in the presence of alkylaluminum and the results are summarized in Table 1 along with the GPC analysis data of the produced polyethylene. The complex **1** supported on Na^+–Mica showed moderate activity for the polymerization of ethylene in the presence of TIBA (Run 1). The activity of the catalyst dramatically increased when Na^+–Mica was replaced with M^{n+}–Mica ($M^{n+} = Mg^{2+}$, Zn^{2+}, and Fe^{3+}) and their activities were approximately 10-fold higher than that of the **1**/Na^+–Mica procatalyst (Runs 1–4). With an increase in the TIBA amount, the activity of the catalyst based on **1**/Mg^{2+}–Mica increased from 4284 (Al/Fe = 500, Run 6) to 7356 kg-PE mol-Fe^{-1} h^{-1} (Al/Fe = 1500, Run 9). The M_n of the produced polyethylenes were within $2.2–2.7 \times 10^4$ except for that obtained by the polymerization at Al/Fe = 1500 ($M_n = 1.7 \times 10^4$, Run 9). Gibson et al. concluded that chain-transfer reaction to an aluminum compound is the operative mechanism for the termination on the basis of the analysis of the chain-end groups of polyethylene.[5] However, no clear evidence for the chain-transfer reaction to the aluminum compound was obtained in the present system.

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Table 1. Polymerization of Ethylene Using **1**/M^{n+}–Mica Procatalyst[a)]

Run	Procatalyst	$P^{b)}$/MPa	Activator	Al/Fe	Activity[c)] Cat-basis	Activity[c)] Fe-basis	$M_n/10^4$	PDI
1	**1**/Na^+–Mica	0.4	TIBA	1000	27	540	2.6	13.9
2	**1**/Zn^{2+}–Mica	0.4	TIBA	1000	324	6476	2.3	15.9
3	**1**/Fe^{3+}–Mica	0.4	TIBA	1000	255	5108	2.2	15.9
4	**1**/Mg^{2+}–Mica	0.4	TIBA	1000	312	6240	2.7	10.2
5	**1**/Mg^{2+}–Mica	0.4	—	—	0	0	—	—
6	**1**/Mg^{2+}–Mica	0.4	TIBA	500	214	4284	2.5	12.2
7	**1**/Mg^{2+}–Mica	0.2	TIBA	500	169	3372	1.7	10.5
8	**1**/Mg^{2+}–Mica	0.7	TIBA	500	301	6020	1.5	11.1
9	**1**/Mg^{2+}–Mica	0.4	TIBA	1500	368	7356	1.7	13.9
10	**1**/Mg^{2+}–Mica	0.4	TEA	500	209	4172	2.6	10.9
11	**1**/Mg^{2+}–Mica	0.4	MAO	500	253	5056	2.4	7.2
12	**1**[d)]	0.4	TIBA	1000	0	0	—	—

a) Polymerization conditions: temp, 60 °C; time, 1 h; cat, 5.0 mg; Solv., hexane (50 mL). b) Ethylene pressure (gauge). c) Cat-basis: g-PE $g\text{-cat}^{-1}\,h^{-1}$, Fe-basis: kg-PE $mol\text{-Fe}^{-1}\,h^{-1}$. d) Homogeneous catalyst.

The effect of the ethylene pressure on the productivity was investigated using a catalyst consisting of **1**/Mg^{2+}–Mica and TIBA (Runs 7–9). Upon increasing the pressure from 0.2 to 0.7 MPa, the productivity increased, whereas no good correlation between the M_n values and the pressure was observed. This unexpected behavior is attributable to the transfer reaction of the β-hydrogen of the polyethylene chain to the monomer at the high monomer concentration. The same behavior was observed during the ethylene polymerization using catalyst consisting of a bis(imino)pyridineiron complex immobilized into fluorotetrasilicic mica interlayers and alkylaluminum.[10]

Moreover, as a characteristic behavior, the polydispersities (PDI) of the obtained polyethylenes were more than 10 and were significantly greater than those obtained by a typical single-site catalyst. In the GPC profile of the produced polyethylene, a high molecular weight fraction was observed as a shoulder peak. Homogeneous polymerization using the bis(imino)pyridineiron–MAO catalyst system also afforded polyethylenes having a bimodal distribution and the ratio of these peaks dramatically changed when the Al/Fe ratio was varied.[2] On the other hand, Schmidt et al. reported that the PDI varied to a higher value with the progress of ethylene polymerization using a supported catalyst consisting of a bis(imino)pyridineiron(II) complex and trimethylaluminum-treated SiO_2, and concluded that a structure change in the active sites took place with time.[11] Although the reason for the large PDI is unclear at this stage, it is thought that PDI was broadened by some competitive chain-transfer reactions caused on plural active species.

Besides fluorotetrasilicic mica, montmorillonite, and saponite were used as a support of bis(imino)pyridine complexes **1** and **2**. The results of the polymerization of ethylene are shown in Figure 2. Both the Sapo- and Mont-based procatalysts readily formed active species upon activation with TIBA, and these activities were much higher than that of the Mica-based analog. Montmorillonite $[Na_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(\mathbf{OH})_2]$ and saponite $[Na_{0.33}Mg_3(Al_{0.33}Si_{3.67})O_{10}(\mathbf{OH})_2]$ have OH groups located on the top of the octahedral sheet. Meanwhile, the Mica, which was synthesized from molten salts containing MgF, does not have OH groups in the ideal structure $[Na(Mg_{2.5})Si_4O_{10}\mathbf{F}_2]$. Weiss et al. reported that Cp_2ZrCl_2 was activated on the sites formed by a reaction between alkylaluminum and Brønsted acid sites (surface OH groups) produced by the acid-treatment of montmorillonite, and the obtained catalyst showed a high activity for α-olefin polymerization.[7] In this catalyst system, the Mont- and Sapo-supported bis(imino)pyridine procatalysts were probably activated by a similar mechanism.

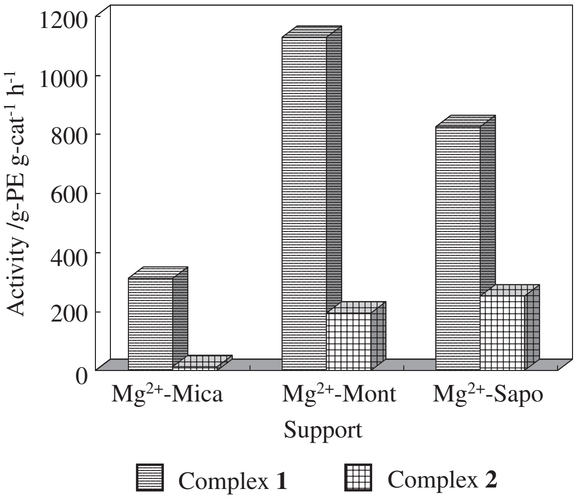

Figure 2. The activity of bis(imino)pyridine complexes supported on various clay minerals. Polymerization conditions: Temp, 60 °C; Ethylene pressure, 0.4 MPa; 1 h, Al(TIBA)/Fe = 1000.

Although the Mont- and Sapo-based procatalysts showed a high activity compared to the Mica-based procatalyst, the activity of the Sapo-based procatalyst decreased to one-third of the fresh procatalyst during storage for 48 h. The deactivation of the Mont-based procatalysts was also observed after one month and the activity decreased to half that of fresh. In contrast, the Mica-based procatalyst maintained its catalyst function for over three months. The reason for the deactivation is due to the reaction of the surface OH groups and bis(imino)pyridine complexes that form inactive μ-oxo species

Table 2. GPC Analysis Results of Polyethylene Obtained Using Sapo- and Mont-Based Procatalyst[a)]

Procatalyst	T/°C	Activity Fe-basis[b)]	$M_n/10^4$	$M_w/10^4$	PDI
1/Mg^{2+}–Mont	60	22568	3.0	58	19
1/Mg^{2+}–Mont	40	9832	1.8	12	7.0
2/Mg^{2+}–Mont	60	3920	4.6	62	14
2/Mg^{2+}–Mont	40	4084	3.4	18	5.2
1/Sapo	60	16512	3.6	51	14
2/Sapo	60	5036	4.4	94	21

a) Polymerization conditions are the same as in Figure 2. b) Fe-basis: kg-PE mol-Fe^{-1} h^{-1}.

reported for supported metallocene complexes.[12] Especially, the Sapo-based catalysts showed extremely shorter lifetimes than the other procatalysts, because the surface area of Mg^{2+}–Sapo (207 m^2 g^{-1}) was much higher than those of Mg^{2+}–Mont (17 m^2 g^{-1}), and Mg^{2+}–Mica (12 m^2 g^{-1}).

The procatalysts consisting of complex **1** and Mg^{2+} ion-exchanged clay minerals (Mg^{2+}–clay) showed higher activity compared with those consisting of complex **2** and Mg^{2+}–clay when TIBA was used as the activator. The difference in the activities between the **1**/Mg^{2+}–clay and **2**/Mg^{2+}–clay was similar to the results obtained by the homogeneous catalyst using MAO.[2] Therefore, the activity of the clay mineral-supported catalyst strongly depends on the nature of the bis(imino)pyridineiron(II) complex.

On the basis of a report by Gibson et al. and other researchers, a catalyst consisting of MAO and complex **2** afforded a high molecular weight polyethylene compared to that consisting of MAO and complex **1**.[4,5] The molecular weights (M_n) and its distributions of the obtained polyethylenes using our procatalysts are summarized in Table 2. The M_n of polyethylene produced during the polymerization at 60 °C using the **2**/Mg^{2+}–Mont procatalyst was slightly higher than that using the **1**/Mg^{2+}–Mont procatalyst.

When the polymerization temperature was decreased from 60 to 40 °C during the polymerization using the catalysts consisting of **2** and Mg^{2+}–Mont, the M_n of the produced polyethylene unexpectedly decreased. The decrease in M_n was also observed in the polymerization using the catalyst consisting of **1** and Mg^{2+}–Mont. From the detailed analysis of the GPC profiles with increasing polymerization temperature, it was found that the PDIs increased with the increase of the M_w. These results strongly suggested that there are at least two active species during the polymerization, and the active species that produced the high molecular weight polyethylene are easily formed at the higher polymerization temperature. This fact clearly indicated that these two active species also caused the expansion of the distribution. The M_w of polyethylene produced using the Sapo-based catalyst was much higher than that produced using the Mont-based catalyst, indicating that the Mg^{2+}–Sapo effectively promoted the formation of the active site that produced the high molecular weight polyethylene (GPC profiles are shown in Supporting Information).

The bis(imino)pyridineiron(II) complex supported on carriers was investigated for the polymerization of ethylene to obtain well-controlled polymer particles from the viewpoint of morphology.[13–16] The catalysts prepared in this study also showed a high processability and afforded well-controlled polyethylene particles (SEM images are shown in Supporting Information).

In conclusion, the saponite- and montmorillonite-supported bis(imino)pyridineiron(II) complex showed a high activity for the polymerization of ethylene compared to the fluorotetrasilicic mica-supported complex when alkylaluminum was used. The obtained polyethylene showed complicated molecular weight distributions, suggesting the existence of both multiple chain-transfer reactions and two types of active species.

Supporting Information

Figures 1–3 are GPC profiles of the produced polyethylenes. Figure 4 is SEM photographs of the supported catalyst and the produced polyethylene particles. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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