Bis(imino)pyridine Iron and Cobalt Complexes Immobilized into Interlayer Space of Fluorotetrasilicic Mica: Highly Active Heterogeneous Catalysts for Polymerization of Ethylene

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Heterogeneous catalysts assembled by the intercalation of a bis(imino)pyridine ligand into late metal ion-exchanged clay mineral interlayers with the simultaneous coordination of the ligand to the interlayer cations were found to be highly active for ethylene polymerization.

A new family of late-metal catalysts, iron and cobalt complexes containing bis(imino)pyridine ligands, were independently discovered by Gibson et al.[1] and Brookhart et al.[2] These iron-based complexes activated with methylaluminoxane showed an extremely high activity for ethylene polymerization compared to the traditional Ziegler–Natta catalysts and produced characteristic polyethylenes having a broad molecular weight distribution. Gibson and co-workers[3,4] continue to investigate the nature of the active sites, effects of the ligand structure on both the catalytic activity and polymer properties and polymerization mechanisms of such complexes.

The homogeneous catalysts based on these iron and cobalt complexes have a significant potential for the production of the characteristic polyethylene; therefore, heterogeneous catalysts having high performances as well as those of a homogeneous catalyst are desired for practical use. In this paper, we report the highly active heterogeneous catalysts (Figure 1) prepared by the direct reaction of the Fe^{3+}- or Co^{2+}-exchanged fluorotetrasilicic mica (host) and bis(imino)pyridine ligand (guest). These catalysts were readily assembled by intercalation of the guest into the host interlayers and subsequent coordination of the guest with the interlayer metal cations.

Late metal ion-exchanged fluorotetrasilicic mica (M^{n+}–Mica, $M^{n+} = Fe^{3+}$ and Co^{2+}) as a host material was prepared by the ion-exchange reaction of Na^+–Mica (Coop Chemical Co., Ltd., ME-100, surface area $= 3.3\,m^2\,g^{-1}$) in aqueous media containing a metal nitrate. After the reaction, the obtained materials were dried overnight at 40 °C, calcined at 200 °C for 4 h, and then dried at 200 °C for 4 h in vacuo. The guests presented in Figure 1 were prepared by the reaction of 2,6-diacetylpyridine with an alkyl-substituted aniline.[4] The procatalysts were prepared by the reaction of the host[5] (1.0 g) with appropriate guests (560 µmol for 1 g of Fe^{3+}–Mica and 840 µmol for 1 g of Co^{2+}–Mica) in 1-butanol at 70 °C for 120 h, washing with the solvent, and then vacuum drying at ambient temperature for 4 h. Ethylene was polymerized on those procatalysts using methylaluminoxane (MAO), triethylaluminum (TEA) or triisobutylaluminum (TIBA) as activators in hexane at 60 °C and at an ethylene pressure (P) of 0.2–0.7 MPa for 1 h. Characterization of the catalysts was performed by powder X-ray diffraction (XRD), infrared spectroscopy (FT-IR), and thermogravimetry-differential thermal analysis (TG-DTA).

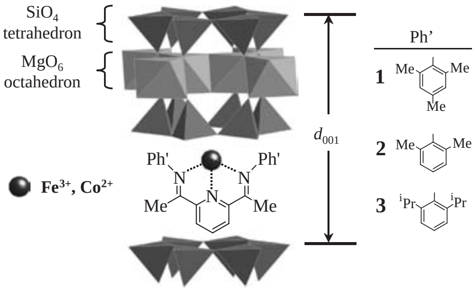

Figure 1. Schematic feature of the catalysts.

The ethylene polymerization results are summarized in Table 1. The procatalyst (**1**/Fe^{3+}–Mica) prepared from ligand **1** (Ph′ = 2,4,6-trimethylphenyl) and Fe^{3+}–Mica in 1-butanol showed an extremely high activity for ethylene polymerization upon activation with not only MAO but also with TEA and TIBA. The morphology of the polymer particles well replicated the sheet-like structure of the starting mica.[5] No significant activity was observed during the polymerization using **2**/Fe^{3+}–Mica in the absence of the aluminum compound, indicating that an activator is necessary for the formation of the active sites. Undoubtedly, the catalyst system combined with Fe^{3+}–Mica (without ligand treatment), and TIBA was completely inactive for the ethylene polymerization. The number-average molecular weight (M_n) of polyethylene obtained using the **1**/Fe^{3+}–Mica catalyst activated with TEA and MAO was lower than that obtained with TIBA. When TEA and MAO were used, chain-transfer reaction to these Al compounds may occur, because that reaction to MAO was observed in the homogeneous polymerization.[3] No significant difference was observed in the molecular weight distributions (MWD $= M_w/M_n$). The melting temperature (T_m) of the produced polyethylene indicated that all the catalysts produced highly linear polyethylenes.

The effects of the phenyl substituents on the catalytic activity and M_n of polyethylene were investigated using the procatalysts having ligand **2** or **3**. The catalyst consisting of ligand **2** (Ph′ = 2,6-dimethylphenyl) and Fe^{3+}–Mica was more active than **1**/Fe^{3+}–Mica, but the activity of **3**/Fe^{3+}–Mica was much lower than that of either one. This order of activity was different from that observed in catalyst systems consisting of the corresponding complex and MAO. Gibson et al. reported that the decrease of steric bulk around the metal center led to both increase of the activity and decrease of the molecular weight.[4] Therefore, the difference of the catalyst performances of **1**- and **2**/Fe^{3+}–Mica is attributed to the steric effects. The catalysts prepared

Table 1. Ethylene polymerization results using built-in catalysts[a]

Entry	Procatalyst[b]	P[c] /MPa	Activator /mmol	Yield of PE/mg	Activity cat-basis[d]	Activity M-basis[d]	M_n[e] /10^4	M_w/M_n[e]	T_m[f] /°C
1	**1**/Fe^{3+}–Mica	0.2	TIBA/0.673	2018	505	931	3.21	9.0	133
2	**1**/Fe^{3+}–Mica	0.2	TEA/0.673	2680	670	1236	1.70	10.0	133
3	**1**/Fe^{3+}–Mica	0.2	MAO/0.673	2750	686	1267	1.98	8.2	134
4	**2**/Fe^{3+}–Mica	0.2	TIBA/0.673	3560	890	1643	1.97	7.1	134
5	**3**/Fe^{3+}–Mica	0.7	TIBA/0.673	71	18	33	2.55	11.3	135
6	**2**/Co^{2+}–Mica	0.7	TIBA/1.02	419	105	164	0.34	23.2	130
7	Fe^{3+}–Mica	0.7	TIBA /0.673	0	—	—	—	—	—
8	**2**/Fe^{3+}–Mica	0.7	—	0	—	—	—	—	—

[a]Polymerizations were performed using 4.0 mg of the procatalyst at 60 °C for 1 h in 50 mL of hexane (solvent). [b]**1** = 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine, **2** = 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine, **3** = 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine. [c]Ethylene pressure (gauge pressure). [d]Cat-basis = g-PE g-cat^{-1} h^{-1}, M-basis = kg-PE mol-M^{-1} h^{-1}. [e]Determined by GPC analysis. [f]Determined by differential thermal analysis (DTA).

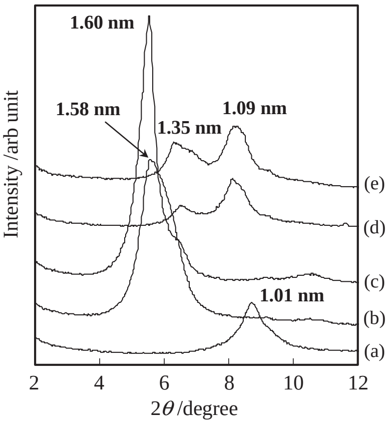

Figure 2. XRD profiles of (a) Fe^{3+}–Mica (before intercalation), (b) **1**/Fe^{3+}–Mica, (c) **2**/Fe^{3+}–Mica, (d) **3**/Fe^{3+}–Mica, and (e) Fe^{3+}–Mica treated with only 1-butanol (without ligand). Samples (b)–(e) were analyzed after drying at 110 °C for 1 h. The values in Figure 2 indicate the basal spacing (d_{001}) including the layer thickness (approximately 1.0 nm).

from Co^{2+}–Mica were less active than those prepared from Fe^{3+}–Mica. Moreover, the Co^{2+}–based catalysts produced polyethylene having a very low M_n and broader MWD.

The XRD profiles[6] were measured for samples of (a) Fe^{3+}–Mica before intercalation, (b) **1**/Fe^{3+}–Mica, (c) **2**/Fe^{3+}–Mica, (d) **3**/Fe^{3+}–Mica, and (e) Fe^{3+}–Mica treated with only 1-butanol under the same preparation conditions, in order to confirm the intercalation of the ligand into the clay mineral interlayers (Figure 2). When Fe^{3+}–Mica was treated with ligands **1** and **2**, the basal spacing, determined on the basis of the diffraction angle of the d_{001} peak, changed from 1.01 nm in (a) to 1.58 nm in (b) and 1.60 nm in (c) with an increase in the peak intensity. Meanwhile, weaker diffraction peaks were observed at d_{001} = 1.35 and 1.09 nm for (e) Fe^{3+}–Mica treated with only 1-butanol (without ligand). These results clearly indicated that ligand molecules **1** and **2** were intercalated into the interlayer spaces and that the lamellae in these procatalysts were stacked with a high degree of regularity. The profile of **3**/Fe^{3+}–Mica (d) is the same as that of (e), indicating that the low activity of **3**/Fe^{3+}–Mica was attributed to the fact that the ligand **3** hardly intercalated into the mica interlayers because of the steric bulk of the isopropyl groups.

Thermal analysis also supported the intercalation of the guest. In the TG-DTA profiles[5] of **1**- and **2**/Fe^{3+}–Mica measured in air, combustion of the incorporated guests was observed around 340 °C with a weight loss, whereas this was not observed in the profiles of **3**/Fe^{3+}–Mica. The formation of the bis(imino)-pyridine–Fe^{3+} complex in the interlayers was identified by FT-IR measurement[5] of the **1**/Fe^{3+}–Mica and related compounds. An adsorption band of $\nu_{C=N}$ derived from the C=N bond coordinated to Fe^{3+} was clearly observed at 1588 cm^{-1} in the FT-IR spectrum.[7]

In conclusion, new heterogeneous catalysts assembling iron and cobalt complexes into mica interlayers show a high activity for ethylene polymerization. This catalyst design can possibly be applied in a wide variety of catalysts as well as ethylene polymerization catalysts by modification of the ligand properties.

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5 Supporting Information (Elemental analysis results and surface area of M^{n+}–Mica, SEM images of Fe^{3+}–Mica and polymer particles, and TG-DTA profiles and FT-IR spectra of procatalysts) is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

6 X-ray powder diffraction profiles were measured with Cu Kα radiation (wave length, 0.15406 nm) at a scan rate of 1.0 deg min^{-1} using a RAD-B system (Rigaku Corporation) equipped with a counter monochlorometer. Before measurement, all samples were placed on a specimen holder and covered with polyester film in a glove box for protection from moisture.

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