Heterogeneous catalysts immobilizing α-Diimine nickel complexes into fluorotetrasilicic mica interlayers to prepare branched polyethylene from only ethylene

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Abstract

The α-diimine nickel (II) complexes immobilized into the clay mineral interlayer were prepared by the reaction of the Ni^{2+} ion-exchanged fluorotetrasilicic mica and the α-diimine ligand.   These procatalysts showed a high catalytic activity for the slurry polymerization of ethylene in the presence of methylalumoxane, triethylaluminum or triisobutylaluminum.   The activity was strongly affected by the solvent used in the preparation and the steric bulk of the ligand.   A high activity (2313 kg-PE mol-Ni^{-1} h^{-1}) was obtained by the polymerization at $50^{\circ}C$ in the presence of triisobutylaluminum using the procatalyst prepared with the [Ar-N=C(CH$_3$)C(CH$_3$)=N-Ar (Ar = 2,6-C$_6$H$_3$(CH$_3$)$_2$)] ligand in acetonitrile.

Key words: Intercalation, Ion exchange, Layered clay minerals.

1. Introduction

Highly active catalysts for the polymerization of ethylene in combination with α-diimine nickel (II) or palladium (II) complexes and methylalumoxane (MAO) were discovered by Brookhart et al [1-4]. This discovery had a profound impact on the polyolefin industry, because these catalysts are capable of not only producing highly branched polyethylene from only ethylene, but also promoting the copolymerization of ethylene with polar comonomers having functional groups, considered to be difficult using the traditional Ziegler-Natta catalysts. Moreover, the active sites in these catalysts are essentially uniform, and the microstructures of polyethylene can be controlled by modification of the ligand backbone. To apply these catalysts to industrial uses, immobilization of the α-diimine Ni (II) complexes on an inorganic carrier have been investigated. SiO_2 [5-11], MCM-41 [12], clay minerals [13-15], $MgCl_2$ [16-18], zeolites [19], and polymers [20] have been reported as carriers in the literature, moreover, recent investigations for the supported catalysts have focused on the nickel (II) complexes chemically bonded with hydroxyl groups on the SiO_2 surface through a functional group introduced in the ligand backbone [5-7, 13].

Recently, we developed novel heterogeneous catalysts that immobilized bis(imino)pyridine iron and cobalt complexes into layered clay mineral interlayers [21]. The catalysts were readily prepared by intercalation of bis(imino)pyridine ligands into the interlayers of the iron (III) or cobalt (II) ions-exchanged fluorotetrasilicic mica with simultaneous coordination of the ligands to the interlayer metal cations. In this paper, we report the heterogeneous catalysts immobilizing α-diimine nickel (II) complexes into fluorotetrasilicic mica interlayers (Fig. 1), which show a high activity for the polymerization of ethylene with an excellent processability.

2. Experimental

The α-diimine ligands were prepared by the method described in the literature [22]. After an ion-exchange reaction of commercially available mica (Na$^+$ form, CO-OP Chemical Corporation) in a nickel (II) nitrate solution, the Ni^{2+} ion-exchanged fluorotetrasilicic mica (Ni^{2+}-Mica) was obtained by calcination at 200ºC for 4 h and then vacuum dried at 200ºC for 4 h under reduced pressure (the amount of incorporated Ni^{2+}-ions = 780 μmol g-Mica^{-1}). The procatalysts were prepared by the reaction of Ni^{2+}-Mica and α-diimine ligands (850 μmol for 1 g of dried Ni^{2+}-Mica) in solvent at 70ºC for 120 h, then washed with the solvent, and vacuum dried at ambient temperature for 4 h.   The activity of the catalysts was evaluated by the slurry polymerization of ethylene at 40-60ºC and 0.4-1.0 MPa for 1 h in the presence of an aluminum compound. X-Ray powder diffraction profiles were measured with Cu-$K\alpha$ radiation (wave length, 0.15406 nm) at the scan rate of 1.0 deg. min^{-1} using Ultima–RINT (Rigaku Corporation). Before measurement, all samples were placed on a specimen holder and covered with polyester film in a glove box for protection from moisture. A scanning electron microscope (SEM, Hitachi Co. Ltd., S-4100) was used for the surface observation of the procatalyst and the polymer particle.

3. Results and Discussion

Table 1 shows the results of the ethylene polymerization. The procatalyst **1** having 2,4,6-trimethylphenyl groups on the nitrogen atoms of the imino group showed a high activity for the polymerization of ethylene in the presence of triisobutylaluminum (TIBA). The active sites are essentially uniform (single site catalyst), though the polydispersity index (PDI) was slightly larger than 2. The relatively large PDI is due to post-polymerization to form low molecular-weight polyethylene. The melting

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temperature of the produced polyethylene was 116ºC, indicating that a branched

polyethylene was formed by the polymerization of only ethylene. The branching

numbers for the polyethylene determined by ^{13}C-NMR was 16 per 1000 carbon atoms

and more than 90% of those was methyl branches. These facts strongly suggested that

the α-diimine Ni^{2+} complex could be effectively inserted into the interlayers of the

fluorotetrasilicic mica.   The procatalyst **2a** was also active for the polymerization in

the presence of TIBA (Entry 2). The activity of **2a** was slightly lower than that of **1** and

no clear differences in *Mn*, PDI, *Tm* and the branching numbers were observed between

the polyethylenes obtained from **1** and **2a**.   The use of triethylaluminum (TEA) instead

of TIBA decreased only the activity (Entry 3).   The catalyst combined with **2a** and

MAO showed the highest activity, but the molecular weight of the obtained

polyethylene decreased (Entry 4). The decrease of the molecular weight is due to the

chain transfer reaction from the active site to MAO.   When the ethylene pressure was

raised, the productivity and the molecular weight were increased with no change in the

PDI (Entry 2, 5, 9). The melting temperature of the polyethylene obtained at a 0.4 MPa

ethylene pressure could not be detected, because the crystallinity decreased with an

increase in the branching numbers. The temperature dependence of the activity during

the polymerization using the procatalyst **2a** was investigated in the temperature range of

40-60ºC.   Remarkably, the productivity at 50ºC was 8 times higher than that at 60ºC,

whereas that at 40ºC was almost same as that at 60ºC (Entry 5, 6, 8).   At 60ºC, the

ethylene consumption rate during the initial stage of the polymerization was faster than

that at 50ºC, but the consumption at 60ºC stopped after 20 min due to catalyst

deactivation. The high productivity was also obtained by the polymerization at 50ºC

using the procatalyst **1** (Entry 7). The molecular weight and melting temperature of the

obtained polyethylenes increased with the decreasing temperature, because the lower

temperature favored the propagation reaction more than the chain transfer reaction (mainly β-hydrogen elimination).

The steric bulk of the phenyl substituents on the nitrogen atoms of the imino groups strongly affected the catalytic activity. The activity of the procatalyst **3** (2,6-diethylphenyl group on the imino nitrogen, Entry 10) was approximately 5 % compared to the procatalyst **2a** (Entry 2), and an extremely low activity was observed when the procatalyst **4** (2,6-diisopropylphenyl group on imino nitrogen, Entry 11) was used. Moreover the solvent used in the catalyst preparation also affected the activity. The procatalyst **2a** (prepared in acetonitrile, Entry 2) showed a 16-times higher activity than that of **2b** (prepared in 1-butanol, Entry 12) and showed a 160-times higher activity than that of **2c** (prepared in toluene, Entry 13). The PDI of PE produced using the procatalyst **2b** was larger than that produced using the procatalyst **2a**. It is considered that the reaction of 1-butanol and the formed Ni^{2+} complex afforded plural species that produced the PE having different chain length.   These dramatic effects of the ligand backbone and the solvent on the activity are caused by the characteristic properties of the clay-based catalysts [21] because the catalytic behavior was not observed in the study of the homogeneous catalyst systems.   As shown in entries 14 and 15, active species were formed by the reaction of the procatalyst and the aluminum compound, and treatment of the Ni^{2+}-Mica with the ligand were indispensable for the formation of the procatalysts.

The SEM images of the procatalyst **2a** and polyethylene obtained by the catalyst were shown in Fig.2. The polyethylene particles were not symmetrical because of the unsymmetrical shape of the Ni^{2+}-mica (Fig.2 (a)), however characteristic morphology of the supported catalysts was observed at the surface of the polymer particles (Fig. 2 (c)). In order to investigate the strength of the interaction between metal complex and mica

support, we attempted to extract soluble metal complexes from the procatalyst **2a** with dichloromethane (DCM) having a high solubility for the α-diimine Ni complex. The activity (2425 kg-PE mol-Ni^{-1} h^{-1}) of the procatalyst washed with DCM was quite same as that (2313 kg-PE mol-Ni^{-1} h^{-1}) of the procatalyst without the treatment in the polymerization at 50°C and 0.7 MPa. Moreover, no reactor fouling was observed during the polymerization using all catalysts in this study. These results clearly show that the metal complex in the present catalysts was strongly held into the mica interlayers and the active species was not extracted with the solvent from the mica interlayers.

To clarify the ligand intercalation into the clay mineral interlayers, the expansion of the basal spacing of the clay-based procatalysts prepared in different solvents were investigated by XRD after their heat treatment at 110ºC for 1 h under vacuum (Fig. 3). The basal spacing of the Ni^{2+}-Mica after drying at 200ºC was approximately 1.0 nm and was equal to the layer thickness of the Mica. The fact indicated that there was no clearance between adjacent layers.   When the Ni^{2+}-Mica was treated with the ligand in toluene (procatalyst **2c**), no significant change in the basal spacing was observed. In contrast, the basal spacing of the procatalyst **2b** (prepared in 1-butanol) was shifted from 1.0 to 1.38 nm. The expansion of the basal spacing (1.39 nm) was more definitely observed in the XRD profiles of the procatalyst **2a** (prepared in acetonitrile). These facts clearly show that the ligand molecules were intercalated into the Ni^{2+} ion-exchanged mica interlayers and the distance between the adjacent layers had increased. To achieve the high activity, the solvent must have two specific properties in this catalyst preparation: an strong polarity is necessary to swell the Ni^{2+}-Mica as mentioned above, and the moderate interaction between the solvent and the metal center reads to high activity because the strong interaction of those prevents the coordination of the ligand. The XRD profiles were also measured for the procatalysts consisting of different ligand

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backbones (Fig. 4). The procatalyst **1** having 2, 4, 6-trimethylphenyl groups on the imino nitrogens showed a strong diffraction peak at $2\theta = 6.50°$ (basal spacing = 1.36 nm), whereas no diffraction peak derived from the intercalation of the ligand was observed in the profiles of the procatalysts **3** and **4**.   The clear difference indicates that the steric bulk of the ligands in the procatalyst **3** and **4** prevented the intercalation of the ligand into the mica interlayer.   Therefore, the low activities of procatalysts **3** and **4** are attributable to a limited number of the Ni^{2+} complexes formed.   The amount of the complexes formed in the interlayer of the Mica was determined by FT-IR measurement of the procatalysts using a calibration factor based on the spectra of the physically mixed samples with specific amounts of the Ni^{2+}-Mica and the ligand.   In the spectrum of the procatalyst **2a**, the absorption band derived from the ligand could not be detected and the amount of the complex formed in the interlayers was estimated to be not more than 20 mol% of the total Ni^{2+} ions because the lower detection limit in this FT-IR measurement was approximately 20 mol%.

Although we do not understand the activation mechanism of the procatalysts in details, it is considered that exfoliation of the mica sheets take place in the early stage of the polymerization and results in the formation of new active sites from the metal complexes placed in the depths of the interlayer space.

In summary, the procatalysts, the α-diimine Ni^{2+} complexes immobilized into the clay mineral interlayer, were prepared by the direct reaction of the Ni^{2+}-ion exchanged fluorotetrasilicic mica and the α-diimine ligand. These procatalysts showed a high catalytic activity for the slurry polymerization of ethylene in the presence of MAO, TEA or TIBA. These catalysts produced polyethylene having a narrow polydispersity (*Mw*/*Mn* = 2-3) and short chain branches similar to those obtained by the homogeneous polymerization. The activity based on the amount of Ni^{2+}-ions placed in the interlayers

of Mica was 2313 kg-PE mol-Ni^{-1} h^{-1} (50ºC and 0.7 MPa in the presence of TIBA).

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Figure captions

Fig.1 Outline of the structure and preparation method of the procatalysts.

Fig.2 SEM images of procatalyst **2a** and polyethylene obtained using its procatalyst.

(a) procatalyst 2a, (b) polyethylene (Entry 6), and (c) high magnification image of (b).

Fig.3 XRD profiles of (a) Ni^{2+}–Mica (after drying at $200\,^{\circ}C$), procatalyst (b) **2c**

(prepared in toluene), (c) **2b** (prepared in 1–butanol), and (d) **2a** (prepared in

acetonitrile). Samples (b)–(d) were measured after vacuum drying at $110\,^{\circ}C$.

Fig.4 XRD profiles of (a) Ni^{2+}–Mica (after drying at $200\,^{\circ}C$), (b) Ni^{2+}–Mica (without

ligand), (c) procatalyst **1,** (d) procatalyst **2a**, (e) procatalyst **3**, and (f) procatalyst **4**.

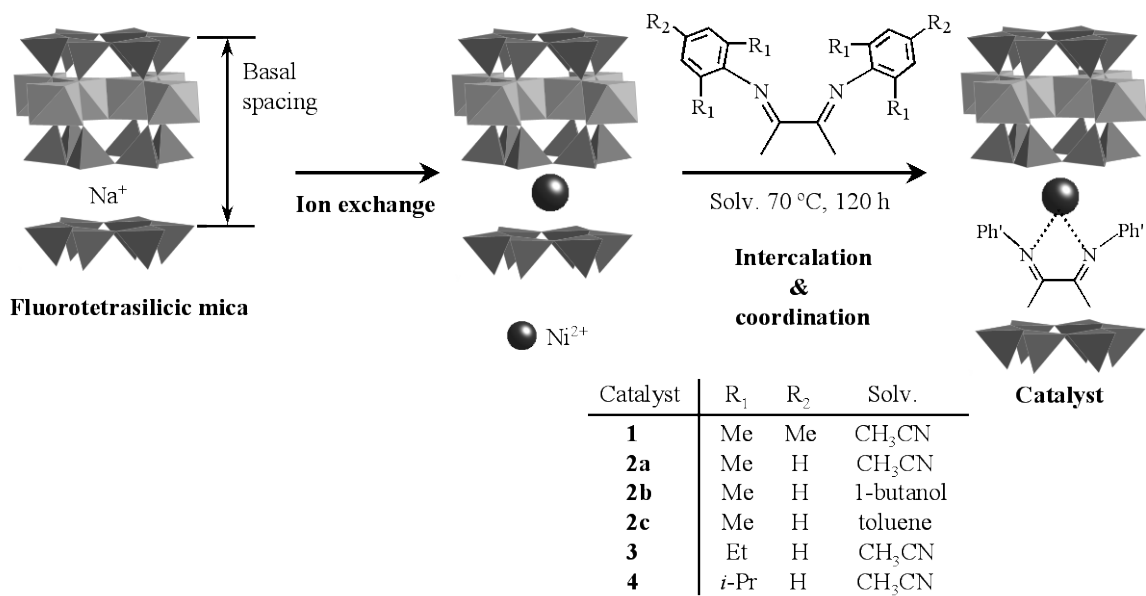Samples (b)–(f) were prepared in acetonitrile and measured after vacuum drying at $110\,^{\circ}$

C.

Catalyst	R_1	R_2	Solv.
1	Me	Me	CH_3CN
2a	Me	H	CH_3CN
2b	Me	H	1-butanol
2c	Me	H	toluene
3	Et	H	CH_3CN
4	i-Pr	H	CH_3CN

Fig. 1 Outline of the structure and preparation method of the procatalysts.

Table 1. Results of slurry polymerization of ethylene with immobilized α-diimine Ni^{2+} complexes[a]

Entry	Cat.	P[b] /MPa	T[c] /°C	Activator[d]	Activity		Mn[f] /10^4	PDI[f]	T_m[g] /°C	Branches[h] /1000C
					Cat[e]	$Metal$[e]				
1	1	1.0	60	TIBA	537	689	9.0	2.6	116	16
2	2a	1.0	60	TIBA	475	609	9.2	2.6	117	17
3	2a	1.0	60	TEA	312	400	8.9	2.6	117	
4	2a	1.0	60	MAO	595	762	5.0	3.0	115	
5	2a	0.7	60	TIBA	238	305	7.5	2.7	113	
6[i]	2a	0.7	50	TIBA	1804	2313	9.8	2.9	120	
7[j]	1	0.7	50	TIBA	1794	2298	–	–	119	
8[i]	2a	0.7	40	TIBA	315	404	12.2	2.9	125	
9	2a	0.4	60	TIBA	84	108	4.2	2.3	nd[k]	
10	3	1.0	60	TIBA	25	32	10.3	2.5	117	
11	4	1.0	60	TIBA	< 1	< 1	–	–	–	
12	2b	1.0	60	TIBA	30	38	7.3	3.5	122	
13	2c	1.0	60	TIBA	3	3	8.4	2.8	121	
14	2a	1.0	60	–	0	0	–	–	–	
15	–	1.0	60	TIBA	0	0	–	–	–	

[a] Polymerization conditions: 120 ml autoclave, 50 ml of hexane, 4.0 mg of procatalyst, 1.02 mmol of activator (Al/Ni = 327), period 1 h. [b] Ethylene pressure. [c] Polymerization temperature. [d] TIBA = triisobutylaluminum, TEA = triethylaluminum, MAO = methylalumoxane. [e] Cat = activity based on catalyst weight (g-PE g-cat^{-1} h^{-1}), $Metal$ = activity based on Ni atom (kg-PE mol-Ni^{-1} h^{-1}). [f] Average number molecular weight (Mn) and polydispersity (PDI = Mw/Mn) were determined by GPC. [g] Melting point (T_m) was determined by DSC. [h] Determined by ^{13}C-NMR. [i] 2.0 mg of catalyst, 0.51 mmol of activator. [j] 1.0 mg of catalyst, 0.43 mmol of activator. [k] Melting point could not be detected.
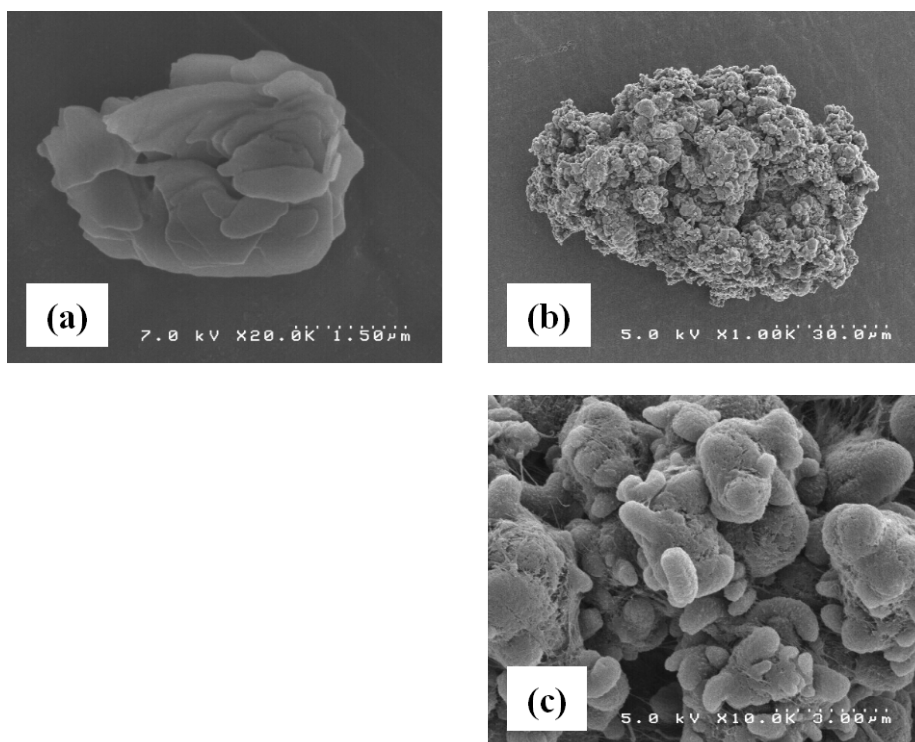
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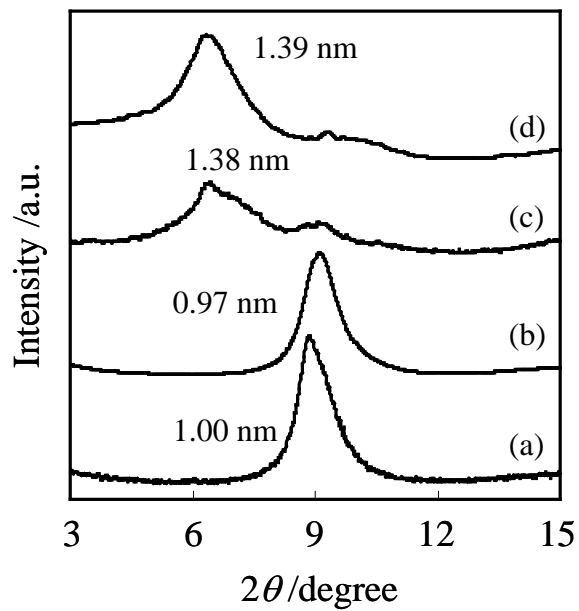
Fig.3 XRD profiles of (a) Ni^{2+}−Mica (after drying at $200\,^{\circ}C$), procatalyst (b) **2c** (prepared in toluene), (c) **2b** (prepared in 1−butanol), and (d) **2a** (prepared in acetonitrile). Samples (b)−(d) were measured after vacuum drying at $110\,^{\circ}C$.
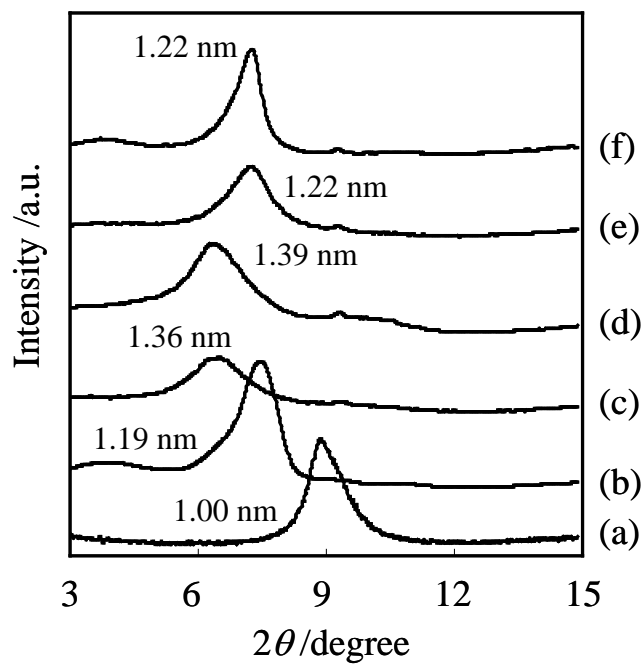
Fig.4 XRD profiles of (a) Ni^{2+}–Mica (after drying at $200\,^{\circ}C$), (b) Ni^{2+}–Mica (without ligand), (c) procatalyst **1,** (d) procatalyst **2a,** (e) procatalyst **3**, and (f) procatalyst **4**. Samples (b)−(f) were prepared in acetonitrile and measured after vacuum drying at $110\,^{\circ}C$.