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Short Communication

Self-assembled heterogeneous late transition–metal catalysts for ethylene polymerization; New approach to simple preparation of iron and nickel complexes immobilized in clay mineral interlayer

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ABSTRACT

To develop heterogeneous catalysts for ethylene polymerization, bis(imino)pyridineiron(III), α-diiminenickel(II), and iminopyridinenickel(II) complexes were immobilized in the clay mineral (montmorillonite, fluorotetrasilicic mica or saponite) interlayers by a one-pot preparation method. In this method, the Fe^{3+}- and Ni^{2+}-exchanged clay minerals as an acid catalyst promoted the ligand formation from a ketone derivative and an aniline derivative, and then the formed ligand simultaneously coordinated to the metal ions located in the clay mineral interlayer. The obtained heterogeneous catalysts showed 100–3,000 g-PE $g\text{-cat}^{-1}\,h^{-1}$ as activities for the ethylene polymerization/oligomerization.

1. Introduction

Since the discovery of nickel and palladium complexes by Brookhart et al. [1] and subsequent development of iron and cobalt complexes by Gibson et al. and Brookhart et al. [2,3], a wide variety of the late transition–metal complexes as a catalyst for the α-olefin polymerization and oligomerization has been actively synthesized [4–12]. In order to use these complexes for the conventional gas-phase and slurry polymerization processes for polyolefin production, the complex must be immobilized on support materials such as SiO_2 and $MgCl_2$ [13–15]. Recently, we developed heterogeneous late transition–metal catalysts which were prepared by the direct reaction of Fe^{3+}, Co^{2+}, or Ni^{2+} ion-exchanged fluorotetrasilicic mica and an appropriate ligand [16–19]. The active component is readily formed by the activation of the procatalyst by a conventional alkyl aluminum compound and showed a high catalytic activity. Moreover, the catalysts also showed an excellent processability, for example, no bleaching of the active species from the mica after washing the procatalyst with solvent [17]. Although the synthesis and purification of the ligand are necessary to prepare these procatalysts having a high catalytic activity, an unstable ligand is hardly isolated because the reaction of the ligand formation is reversible.

As an excellent method for the preparation of the nickel complexes bearing the unstable iminopyridine or α-diimine ligand, the in-situ preparation of the nickel complex from a ketone derivative and an aniline derivative in the presence of $NiCl_2$ was successfully developed [20–23]. Meanwhile, transition metal ion-exchanged clay minerals are known to possess Lewis acidity [24–27]; these effectively promote the reaction between a ketone derivative and an aniline derivative to afford imines, which is catalyzed by an acid.

These results led us to the development of a new simple and effective procedure to prepare an immobilized late transition–metal complex as a heterogeneous catalyst. As a typical example, the one-pot preparation of the heterogeneous bis(imino)pyridineiron(III) procatalyst from 2,6-diacetylpyridine (**K1**), 2,4, 6-trimethylaniline (**A1**), and Fe^{3+} ion-exchanged mont is illustrated in Fig. 1.

2. Experimental section

All chemicals were purchased from Kanto Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd. Montmorillonite (mont) as a typical clay mineral was obtained from the Clay Science Society of Japan. Synthetic saponite (sapo) and fluorotetrasilicic mica (mica) were supplied from the Clay Science Society of Japan and COOP Chemical Co., Ltd., respectively. The solvent used for the procatalyst preparation and the ethylene polymerization/oligomerization was degassed by N_2 bubbling, then dehydrated over 400 °C-dried MS-13× before use.

The ion exchange reaction of the Na^+-clay with M^{n+} (Ni^{2+}- or Fe^{3+}) ions was performed according to the procedure described in the Supporting information (Fig. S1). The prepared ion exchanged-clays were

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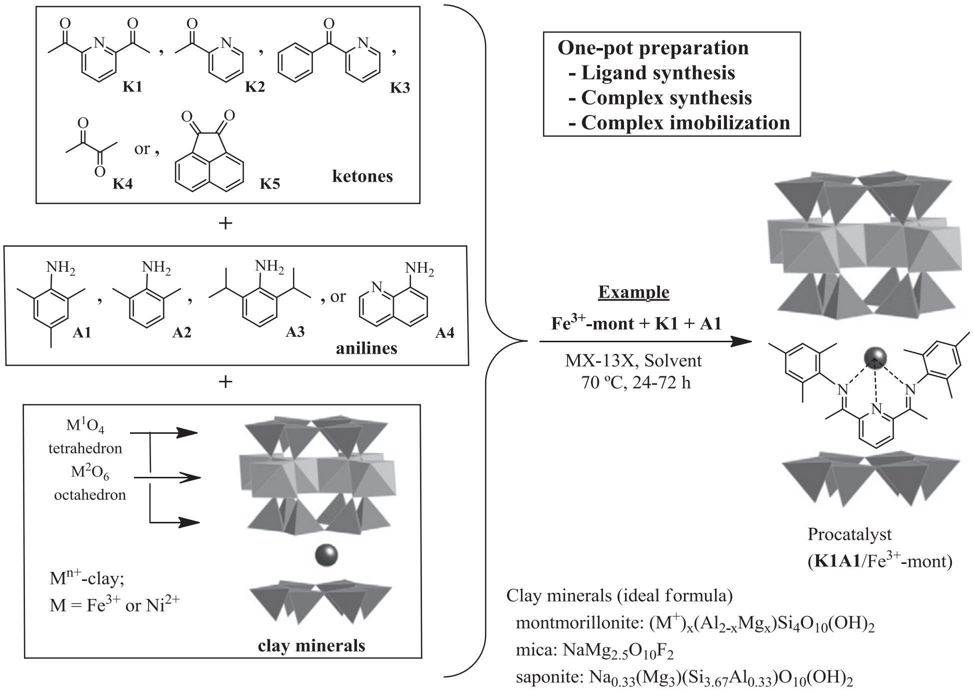

Fig. 1. One-pot preparation of heterogeneous late transition–metal catalysts.

dried at 200 °C for the M^{n+}-mica or at 300 °C for the M^{n+}-mont and M^{n+}-sapo. The composition determined by an XRF measurement is summarized in the Supporting information (Table S1). The preparation of the procatalysts was done by the reaction of the dried M^{n+}-clay, a ketone derivative (**K1–5**), and an aniline or quinoline derivative (**A1–4**) in a solvent (EtOH, CH_3CN, or toluene) under reflux conditions for 24–72 h using a Schlenk flask equipped with a Soxhlet extractor that contained the dried MX-13X. An illustration of the apparatus and preparation procedure are indicated in the Supporting information (Figs. S2 and S3), respectively. After the preparation, almost all the solvent was removed using a syringe, and then the solid was successively washed with the reaction solvent, toluene, and hexane in order to remove the free ligand. The procatalysts were obtained after drying the solid product at ambient temperature under reduced pressure.

The ethylene polymerization/oligomerization was conducted using a 120-ml autoclave equipped with a magnetic stirrer. *n*-Hexane (50 ml), the prepared procatalyst, and an alkylaluminum compound were successively added to an autoclave under a nitrogen atmosphere. The autoclave was placed in the water bath that was maintained at the reaction temperature, and then it was flushed and pressurized with ethylene up to the desired level. The polymerization/oligomerization was performed with a continuous supply of ethylene. The produced polyethylene was recovered, dried, and weighed in order to determine the catalytic activity. The detailed procedure is reported in a previous paper [19]. The properties of the obtained PE were determined using differential scanning calorimetry (DSC, Shimadzu Corporation, DSC-60) and gel permeation chromatography (GPC, ALC/GPC 150C, Waters Corporation). The ^{13}C NMR spectra of the produced PEs were measured using Bruker BioSpin K.K., Avance III 300 spectrometer.

Table 1
Ethylene polymerization using the **K1**(**A1–3**)/Fe^{3+}-clay procatalysts prepared by one-pot preparation.

Run	Procatalyst preparation [a]				Polymerization [b]		PE property [c]	
	M^{n+}-clay	A	Solvent	Time/h	R_3Al	Activity	$M_n/10^4$	PDI
1	Fe^{3+}-mont	**A1**	EtOH	24	TEA	1640	3.50	11.0
2	Fe^{3+}-mont	**A1**	CH_3CN	24	TEA	2000	3.88	9.1
3	Fe^{3+}-mont	**A1**	Toluene	24	TEA	180	2.41	12.1
4	Fe^{3+}-mont	**A1**	EtOH	72	TEA	2950	3.78	12.0
5	Fe^{3+}-mont	**A2**	EtOH	24	TEA	1760	3.43	9.3
6	Fe^{3+}-mont	**A1**	EtOH	24	TIBA	380	3.15	12.9
7 [d]	Fe^{3+}-mont	**A3**	EtOH	72	TEA	70	2.62	17.1
8	Fe^{3+}-mica	**A1**	EtOH	24	TEA	990	2.98	12.6
9	Fe^{3+}-sapo	**A1**	EtOH	24	TEA	830	2.93	11.4
10 [e]	Fe^{3+}-mont	**A1**	EtOH	24	TEA	0	–	–
11 [f]	Fe^{3+}-mont	–	EtOH	24	TEA	0	–	–
12 [g]	**L1**/Fe^{3+}-mont		CH_3CN	120	TEA	5170	NA	NA

[a] **K1**/Fe^{3+} = 100 μmol g-clay^{-1} (Entries 1–6 and 8–11) and 560 μmol g-clay^{-1} (Entry 7).

[b] Polymerization conditions: 120 ml autoclave, solvent = hexane (50 ml), procatalyst = 1.0 mg, polymerization temperature = 60 °C, polymerization time = 1 h, R_3Al = 0.30 mmol, ethylene pressure = 0.4 MPa (gauge), Activity = g-PE g-cat^{-1} h^{-1}, NA = not analyzed.

[c] M_n = average number molecular weight, PDI = polydispersity index (M_w/M_n).

[d] Procatalyst = 2.0 mg, TEA = 1.12 mmol.

[e] Procatalyst prepared with Fe^{3+}-mont and only **A1**.

[f] Procatalyst prepared with Fe^{3+}-mont and only **K1**.

[g] Prepared by an ordinary method using 2,6-(2,4,6-Me_3Ph-N = C(Me))$_2$pyridine (**L1**) and Fe^{3+}-mont.