Effect of "topotactic" reduction product of molybdenum disulfide on catalytic activity of metallocene catalyst for olefin polymerization

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Abstract

N,N-Dimethylanilinium salt of molybdenum disulfide (MoS_2) was developed as a novel cocatalyst for metallocene catalysts. The cocatalyst is composed of N,N-dimethylanilinium ion as a cationic part and "topotactic" reduction product of MoS_2, obtained by acquisition of an electron by neutral host lattice of MoS_2 without structural alteration, as an anionic part. In ethylene polymerization, addition of the N,N-dimethylanilinium salt of MoS_2 to the bis(indenyl)zirconium dichloride (Ind_2ZrCl_2)/triethylaluminum (Et_3Al) catalyst improved the catalytic activity per mmol of Ind_2ZrCl_2. The catalytic activity of this system activated by addition of the cocatalyst depended significantly on the amount of the cocatalyst and the N,N-dimethylanilinium ion content in the cocatalyst. Poly(ethylene) and poly(ethylene-co-1-hexene) obtained with the metallocene catalyst activated by addition of the cocatalyst have typical features such as narrow molecular weight distribution and narrow composition distribution like polymers obtained with conventional metallocene catalysts.
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1. Introduction

Metallocene/alkylaluminum catalysts have long been employed as a model of heterogeneous Ziegler–Natta polymerization catalysts for mechanistic studies [1]. Early 1960, Breslow and Newburg proposed a cationic complex $[Cp_2TiEt^+][AlEtCl_3{}^-]$ as an active species in the bis(cyclopentadienyl)titanium(IV) dichloride (Cp_2TiCl_2)/diethylaluminum chloride ($AlEt_2Cl$) catalyst system on the basis of UV-Vis spectroscopic and chemical studies [2,3]. However, this metallocene catalyst has not attracted much attention because of its poor catalytic activity. Accidental observation that moisture significantly improved the catalytic activity of Group 4 metallocene derivatives, for example, Cp_2ZrMe_2/alkylaluminum in ethylene and propylene polymerizations led to a discovery of methylaluminoxane (MAO) as a cocatalyst [1,4]. This finding aroused commercial and scientific interests in the metallocene catalyst. The role of a Lewis acidic MAO in these polymerizations was proposed to be abstraction of an alkyl group and formation of a formally three-coordinate cation, i.e. $[Cp_2ZrMe^+]$ [5,6]. The formation of such a cationic metallocene

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compound stimulated researchers to investigate the ionic compounds of the $[Cp'_2MR^+][A^-]$ type, where Cp', M, R, and A^- are a substituted or unsubstituted cyclopentadienide, a Group 4 metal, an alkyl group, and a counter anion, respectively, and it was found that the activity of these compounds was highly sensitive to the nature of the counter anion. Unfortunately, preparation of effective and versatile catalysts has been limited by lack of counter anions suitable for metallocene cation with strong Lewis acidity. The use of hexafluorophosphate (PF_6^-) or tetraphenylborate (BPh_4^-) anions for "naked" Cp'_2MR^+ cations result in anion degradation [7] or led to poor anion lability [8]. Recently, the Cp'_2MCl_2/alkylaluminum catalyst activated with a tetrakis(pentafluorophenyl)borate $(B(C_6F_5)_4^-)$-based salt was reported to be as active as the Cp'_2MR_2/MAO catalyst [9,10]. The $B(C_6F_5)_4^-$-based salt as a cocatalyst has been shown to convert Cp'_2MR_2 into the Cp'_2MR^+ by protolysis or alkyl abstraction and to provide the cationic species with $B(C_6F_5)_4^-$ as a counter anion [10–12]. The active species in the Cp'_2MCl_2/alkylaluminum catalyst activated with $B(C_6F_5)_4^-$-based salt was supposed to be a salt of Cp'_2MR^+ with $B(C_6F_5)_4^-$ [10].

Recently, we found that the salt of ammonium ion and anion obtained by "topotactic" reduction is a significantly effective cocatalyst in metallocene catalysts for the ethylene polymerization [13]. The "topotactic" reduction can be defined as the bulk reaction of an electronically conducting host lattice (Z) with vacant lattice sites (□) with electrons [Eq. (1)] [13].

$$xA^+ + xe^- + \Box_x[Z] \rightarrow (A^+)_x[Z]^{x-} \qquad (1)$$
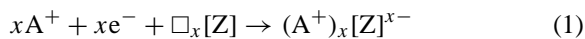
The electrons provided by concurrent chemical or electrochemical reactions enter into the conduction band of the host lattice. At the same time, an equivalent amount of mobile guest cation (A^+) of electrolyte might diffuse from the host–electrolyte interface to the vacant lattice site of the host lattice. Therefore, basic structural integrity of the host matrix is retained during the course of the reaction (topotactic process). The solid in the reduced state is shown as a macroanion matrix $[Z]^{x-}$ with intercalated mobile guest cation A^+. Here, on the basis of the structural characteristics, the host lattice (Z) may be divided into the following four kinds of categories: three-dimensional (3D) system, two-dimensional (2D) system, one-dimensional (1D) system, and molecular solid [13].

In this paper, we described the synthesis of a cocatalyst based on molybdenum disulfide (MoS_2) as a 2D host lattice system, the effect of the cocatalyst on catalytic activity of a metallocene catalyst, and influence of guest cation content in the cocatalyst for the ethylene polymerization. Moreover, the ethylene/1-hexene copolymerization with this catalyst system was investigated.

2. Experimental

2.1. Materials

Molybdenum disulfide $(MoS_2;$ 99.5%, Kishida Chemicals Co.), n-butyllithium (BuLi) solution in n-hexane (1.6 M, Kanto Chemicals Co.), 25% aqueous ammonia (Wako Pure Chemical Industries Ltd.), triethylaluminum (Et_3Al) solution in toluene (20 wt.%, TOSOH Fine Chem. Co.), toluene (Kanto Chemicals Co.), and ethylene (purity 99.99%, produced by Sumitomo Seika Co.) were used without further purification. N,N-Dimethylanilinium chloride $(Ph(Me)_2N\cdot HCl)$ was prepared by addition of hydrogen chloride to N,N-dimethylaniline in diethyl ether. Bis(indenyl)zirconium dichloride (Ind_2ZrCl_2) was synthesized according to the procedure reported in literature [14]. 1-Hexene (Mitsubishi Chemical Co.) was dried over calcium hydride and then distilled.

2.2. N,N-Dimethylanilinium ion intercalated MoS₂

N,N-Dimethylanilinium ion intercalated MoS_2 was prepared according to the procedure reported previously [15,16]. MoS_2 powder was soaked in n-butyllithium solution in n-hexane under nitrogen atmosphere at room temperature to give a Li^+ intercalated MoS_2 (Li_xMoS_2), which was collected by filtration, washed repeatedly with n-hexane, and then dried at room temperature under reduced pressure until a constant weight is obtained. Then, the resulting Li_xMoS_2 powder was soaked in aqueous ammonia, $tert$-butylamine, or water under nitrogen atmosphere and then washed with water to give corresponding hydrates $((Li^+)_{x-m}(H_2O)_y[MoS_2]^{(x-m)-})$, which was collected by filtration. The obtained hydrates were suspended in water and the resulting mixture was added to aqueous $Ph(Me)_2N\cdot HCl$ solution under

nitrogen atmosphere at room temperature. The deposited product ($[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$) was collected, washed repeatedly with water, and then dried at room temperature under reduced pressure until a constant weight is obtained.

2.3. Polymerization procedure

Ethylene polymerization and ethylene/1-hexene copolymerization were carried out in a 2 l autoclave equipped with a magnetic stirrer, a thermometer, and various inlet tubes at 80 °C. The autoclave was flushed several times with nitrogen, filled with 0.5 l of toluene or 1.2 l of *n*-hexane, and the catalyst components were added into it. For the copolymerization, 1-hexene was added. Polymerization was immediately initiated by the introduction of ethylene at 2.0 or 0.6 MPa pressure. Ethylene was continuously supplied to keep the pressure constant during polymerization. After a given polymerization time, ethanol was added into the reaction mixture to terminate the polymerization and the gas feed was stopped. Unreacted gas was released and the resulting mixture was added to the ethanol. The solid poly(ethylene) or poly(ethylene-*co*-1-hexene) was recovered by filtration, adequately washed with large amount of ethanol, and dried at 70 °C under reduced pressure until a constant weight is obtained.

2.4. Characterization

The X-ray diffraction (XRD) measurements of *N,N*-dimethylanilinium ion intercalated MoS_2 and hydrate of Li_xMoS_2 ($((Li^+)_{x-m}(H_2O)_y[MoS_2]^{(x-m)-})$) were performed on a Mac Science MXP[18] diffractometer using Cu Kα radiation (40 kV and 150 mA) at an instrumental resolution of 0.02° in 2θ and a scanning rate of 2 °/min. The Li content in Li_xMoS_2 was measured by inductively coupled plasma (ICP) atomic emission spectrophotometer (DERIVATIVE ICPAES UOP-1 (M) MK-II, manufactured by KYOTO-KOKEN Inc.). The amounts of ammonium ion were determined by CHN elemental analysis (Yanaco CHN CORDER MT-5). Molecular weight and molecular weight distribution of the polymers were measured on a gel permeation chromatography (GPC) apparatus (Waters Model 150C ALC/GPC) with a GMH-HR-H (S) column (TOSOH Co.) at a temperature of 145 °C, calibrated with standard

polystyrene as a reference, using *o*-dichlorobenzene as an eluent. Differential scanning calorimetry (DSC) measurement was performed by a SEIKO DSC-200 at a heating rate of 10 °C/min. Cross-fractionation chromatography (CFC) was conducted using a Mitsubishi Petrochemical CFC T-101.

3. Results and discussion

3.1. Preparation of N,N-dimethylanilinium ion intercalated MoS₂

Intercalation of *N,N*-dimethylanilinium ion ($Ph(Me)_2NH^+$) into MoS_2 was carried out in a procedure similar to that reported by Schöllhorn and Weiss [16] as shown in Scheme 1 [15].

The topotactic reduction of MoS_2 with BuLi was carried out at different $[BuLi]/[MoS_2]$ ratios and the results are summarized in Table 1. The Li^+ content in the Li^+ intercalated MoS_2 (Li_xMoS_2) increased with increasing $[BuLi]/[MoS_2]$ ratio.

The Li^+ present in the interlayer of Li_xMoS_2 obtained was hydrated by the treatment of Li_xMoS_2 with aqueous ammonia at −30 °C, followed by the treatment of water. Fig. 1(d) shows a X-ray powder diffraction (XRD) pattern of a pure MoS_2. The peak of 2θ = 14.40° is assigned to a (0 0 1) reflection of the pure MoS_2. The basal spacing (*d*), i.e. the distance between neighboring MoS_2 layers was 6.15 Å, identical to that reported by Schöllhorn and co-workers [17]. The XRD pattern of the hydration product in a wet state obtained at a $[BuLi]/[MoS_2]$ ratio of 2.0 is shown in Fig. 1(a). The peaks of 2θ = 7.24° and 14.48° are assignable to (0 0 1) and (0 0 2) reflections of the hydrated product, respectively. The (0 0 1) reflection is shifted to a lower angle than that of the pure MoS_2

Table 1
Preparation of intercalated product, Li_xMoS_2, by the reduction[a] of MoS_2 with *n*-butyllithium

[BuLi]/[MoS₂]	Products	
	Li (wt%)	Composition
0.5	2.4	$Li_{0.6}[MoS_2]$
0.8	3.3	$Li_{0.8}[MoS_2]$
2.0	4.9	$Li_{1.2}[MoS_2]$

[a] Reaction conditions: time, 18 h; solvent, hexane; temperature, 20 °C.
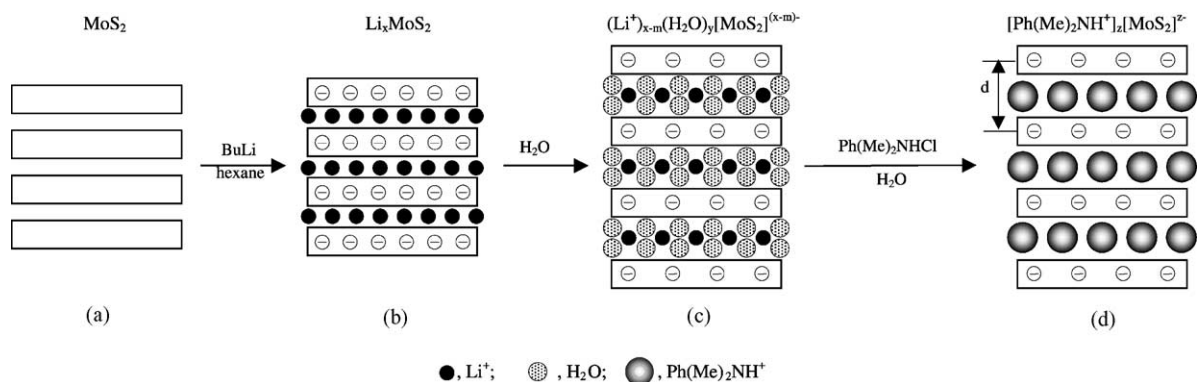
Scheme 1. Scheme of formation of *N,N*-dimethylanilinium ion intercalated MoS_2: (a) MoS_2, (b) lithium ion intercalated MoS_2, (c) hydrated lithium ion intercalated MoS_2, and (d) *N,N*-dimethylanilinium ion intercalated MoS_2.

and the basal spacing (d) increases to 12.20 Å. The interlayer expansion (Δd) of 6.05 Å corresponds to a structure with bimolecular layers of water between MoS_2 sheets and the peak corresponding to a (0 0 1) reflection of a pure MoS_2 disappears completely, suggesting co-intercalation of water molecules with Li^+ into almost all interlayer space of MoS_2. The XRD patterns of hydration products in the wet state obtained at the [BuLi]/[MoS_2] ratios of 0.8 and 0.5 are shown in Fig. 1 (b) and (c), respectively, where two reflections assignable to the hydrated product ((Li^+)$_{x-m}$(H_2O)$_y$[MoS_2]$^{(x-m)-}$) and a pure MoS_2, respectively, are observed. The relative strength of the peak ($2\theta = 7.2°$) due to a (0 0 1) reflection of the hydrated product to that ($2\theta = 14.4°$) of pure MoS_2 increased with increasing [BuLi]/[MoS_2] ratio.

Cation exchange reaction of the hydrated Li^+ in the interlayer space to Ph(Me)$_2$NH$^+$ was performed by contacting the hydration product ((Li^+)$_{x-m}$(H_2O)$_y$ [MoS_2]$^{(x-m)-}$) with Ph(Me)$_2$N·HCl in water. The XRD patterns (Fig. 2) of the cation exchanged products in a wet state are approximately the same as those of the products obtained by the hydration. In Table 2 are summarized the results of XRD and elementary analysis of the products in a dry state obtained by cation exchange reaction to Ph(Me)$_2$NH$^+$.

On drying at room temperature, the basal spacing (d) of the cation exchanged products decreased slightly from 12.20 Å to 11.72–11.97 Å, while the basal spacing of (Li^+)$_{x-m}$(H_2O)$_y$[MoS_2]$^{(x-m)-}$ decreased from 12.20 to 9.20 Å. These basal spacings suggest the existence of Ph(Me)$_2$NH$^+$ in the interlayer space of cation exchange product. The content of Ph(Me)$_2$NH$^+$ calculated from H (wt.%) by elementary analysis is in agreement with that from C or N (wt.%), indicating the absence of water in cation exchange product in a dry state. No Li^+ could be detected for all products (by ICP measurement), either. These results indicate that

Table 2

Characterization of *N,N*-dimethylanilinium ion intercalated MoS_2 obtained under various reduction conditions

Reduction conditions		d^a (Å)	Δd^b (Å)	Products			Composition
[BuLi]/[MoS_2]	Time (h)			C (wt.%)	H (wt.%)	N (wt.%)	
0.5	18	11.97	5.83	5.83	0.61	0.72	[Ph(Me)$_2$NH$^+$]$_{0.09}$[MoS_2]$^{0.09-}$
0.8	18	11.90	5.76	9.12	1.16	1.34	[Ph(Me)$_2$NH$^+$]$_{0.14}$[MoS_2]$^{0.14-}$
2.0	18	11.72	5.58	10.50	1.32	1.55	[Ph(Me)$_2$NH$^+$]$_{0.20}$[MoS_2]$^{0.20-}$

Reduction conditions: solvent, *n*-hexane; temperature, 20 °C. Hydration conditions: ammonia water, 25%; temperature, −30 °C; time, 3 h. Ion exchange conditions: solvent, water; Ph(Me)$_2$N·HCl, 87 mmol/L; temperature, 20 °C; time, 18 h.

[a] d, interlayer spacing.

[b] $\Delta d =$ d(Ph(Me)$_2$NH$^+$ intercalated MoS_2) − d(MoS_2).
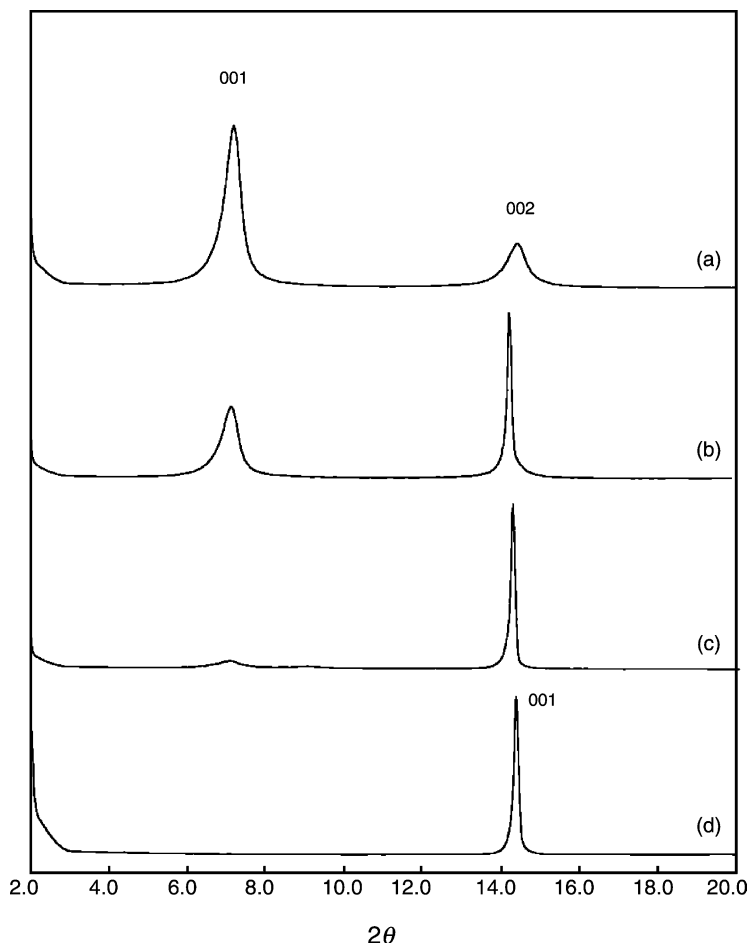
Fig. 1. The XRD patterns of hydration products of Li^+ intercalated MoS_2 obtained at $[BuLi]/[MoS_2]$ ratios of: (a) 2.0, (b) 0.8, (c) 0.5, and (d) pure MoS_2.

only $Ph(Me)_2NH^+$ is present in the interlayer space of the cation exchange product and that the hydrated Li^+ is not. The content of $Ph(Me)_2NH^+$ increased with increasing $[BuLi]/[MoS_2]$ ratio. These results suggest that in the cation exchange product with the $[BuLi]/[MoS_2]$ ratio of 2.0, $Ph(Me)_2NH^+$ is intercalated in all interlayer space of MoS_2, but in those with $[BuLi]/[MoS_2]$ ratios of 0.5 and 0.8, $Ph(Me)_2NH^+$ is partly intercalated in interlayer space of MoS_2.

The effect of the hydration conditions (soaking with aqueous ammonia, aqueous *tert*-butylamine, or water) on the $Ph(Me)_2NH^+$ content in cation exchange product was investigated and the results are summarized in Table 3.

The reduction product obtained at the $[BuLi]/[MoS_2]$ ratio of 2.0 was used as a starting material. The XRD patterns of all $Ph(Me)_2NH^+$ intercalated MoS_2 showed no peak due to pure MoS_2, indicating intercalation of the $Ph(Me)_2NH^+$ in all interlayer space of MoS_2. By the hydration reaction with aqueous *tert*-butylamine ($pK_b^{25} = 3.47$), which is more basic than aqueous ammonia ($pK_b^{25} = 4.75$), the $Ph(Me)_2NH^+$ content in cation exchange product increased from 0.20 to 0.23 mol/mol of MoS_2. By the treatment with water the $Ph(Me)_2NH^+$ content decreased to 0.17 mol/mol of MoS_2. On the other hand, direct treatment with aqueous $Ph(Me)_2N \cdot HCl$ without hydration reaction provided the material with
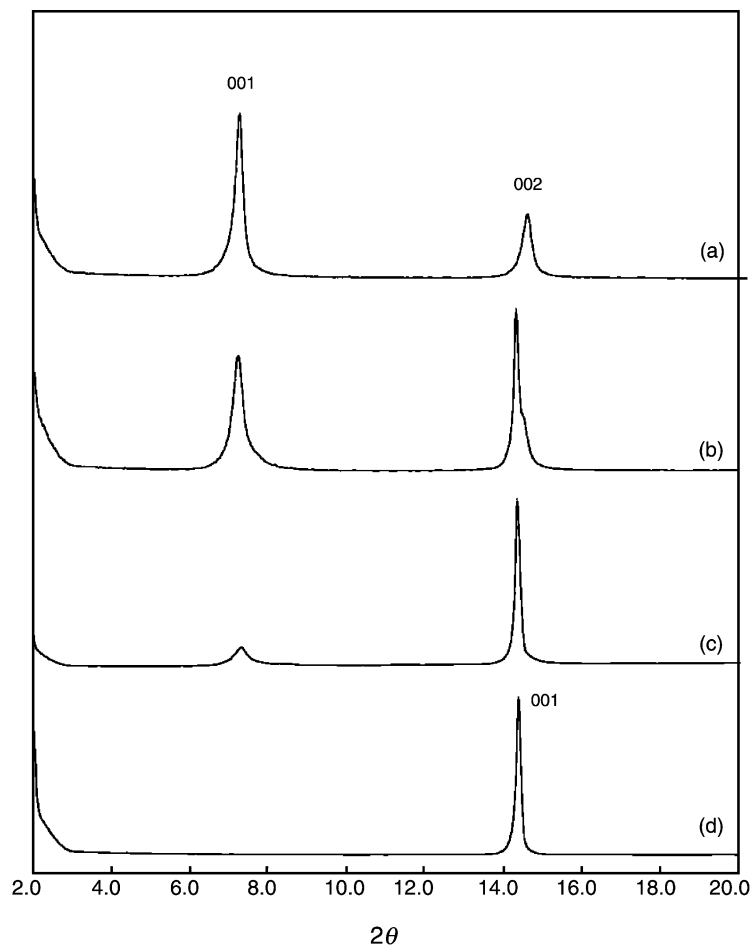
Fig. 2. The XRD patterns of cation exchange products from hydrated Li^+ to $Ph(Me)_2NH^+$ in hydration products of Li^+ intercalated MoS_2 obtained at $[BuLi]/[MoS_2]$ ratios of: (a) 2.0, (b) 0.8, (c) 0.5, and (d) pure MoS_2.

Table 3
Characterization of N,N-dimethylanilinium ion intercalated MoS_2 obtained under various hydration conditions

Hydration conditions		Products					
Lewis base (mol l^{-1})	Temperature (°C)	d^a (Å)	Δd^b (Å)	C (wt.%)	H (wt.%)	N (wt.%)	Composition
tBuNH$_2$ 3.8	5	11.68	5.54	11.60	1.47	1.70	$[Ph(Me)_2NH^+]_{0.23}[MoS_2]^{0.23-}$
NH$_3$ 13.3	−30	11.72	5.58	10.50	1.32	1.55	$[Ph(Me)_2NH^+]_{0.20}[MoS_2]^{0.20-}$
None 0	5	12.80	6.66	9.00	1.14	1.34	$[Ph(Me)_2NH^+]_{0.17}[MoS_2]^{0.17-}$
– –	–	10.02	3.88	6.70	0.85	0.97	$[Ph(Me)_2NH^+]_{0.12}[MoS_2]^{0.12-}$

Reduction conditions: solvent, n-hexane; $[BuLi]/[MoS_2] = 2.0$; temperature, 20 °C; time, 18 h. Hydration conditions: time, 3 h. Ion exchange conditions: solvent, water; $Ph(Me)_2NHCl$, 87 mmol/L; temperature, 20 °C; time, 18 h.

[a] d, interlayer spacing.
[b] $\Delta d = d(Ph(Me)_2NH^+$ intercalated $MoS_2) - d(MoS_2)$.

$Ph(Me)_2NH^+$ content as low as $0.12\,mol/mol$ of MoS_2 and the basal spacing of $10.0\,\text{Å}$. When alkali metal (M) intercalated MoS_2 was contacted with water, oxidation reaction of $[MoS_2]^{x-}$ to $[MoS_2]^{(x-m)-}$ takes place by the removal of electron and simultaneously the hydrated product is formed (Eq. (2)) [16]. The alkali metal content in the interlayer space of MoS_2 decreases from x to $x-m$ with this oxidation.

$$(M^+)_x[MoS_2]^{x-} + (m+y)H_2O$$
$$\rightarrow (M^+)_{x-m}(H_2O)_y[MoS_2]^{(x-m)-}$$
$$+ mM^+ + mOH^- + (m/2)H_2 \qquad (2)$$
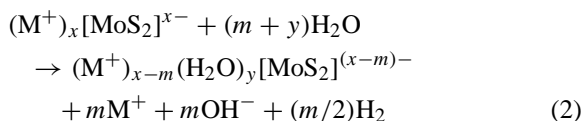
The alkali metal content in the hydrated product decreases slowly by washing with water. This oxidation is strongly pH-dependent and further proceeds with increasing H_3O^+ concentration [18]. Therefore, by the treatment of the hydrated product with dilute mineral acid, pure MoS_2 was recovered quantitatively [16]. We speculated that increase in the basicity in hydration reaction by the addition of Lewis base suppresses effectively lowering of pH prior to the ion exchange with $Ph(Me)_2NH^+$, resulting in the increase in the $Ph(Me)_2NH^+$ content. This speculation was supported by the significant decrease in the $Ph(Me)_2NH^+$ content by direct contact of the reduction product with acidic aqueous N,N-dimethylanilinium chloride without hydration reaction.

3.2. Ethylene polymerization with metallocene catalyst activated with N,N-dimethylanilinium ion intercalated MoS₂

Bis(indenyl)zirconium dichloride (Ind_2ZrCl_2)/triethylaluminum (Et_3Al) catalysts activated with $Ph(Me)_2NH^+$ intercalated MoS_2, derived from re-

duction products at $[BuLi]/[MoS_2]$ ratios of 0.5, 0.8, and 2.0, were tested for their potential as ethylene polymerization catalysts at $80\,^\circ C$ under ethylene pressure of 0.6 or $2.0\,MPa$. The results are summarized in Table 4 for the ethylene polymerization by using the Ind_2ZrCl_2/Et_3Al catalyst activated with various amount of $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ derived from reduction product at the $[BuLi]/[MoS_2]$ ratio of 0.8 under ethylene pressure of $2.0\,MPa$ (run no. 1–5) and $0.6\,MPa$ (run no. 6) for $60\,min$.

Addition of $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ to the Ind_2ZrCl_2/Et_3Al $(1/500\,\mu mol)$ catalyst enhanced the catalytic activity per mmol of Ind_2ZrCl_2 and the increase in the amount of $[Ph(Me)_2NH^+]_{0.14}$ $[MoS_2]^{0.14-}$ improved the catalytic activity. These results indicate that $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ functions as a cocatalyst for the Ind_2ZrCl_2/Et_3Al catalyst. The molecular weight (M_n) of poly(ethylene) produced by this catalyst system was approximately the same as that obtained by the Ind_2ZrCl_2/Et_3Al catalyst itself. The index of polydispersity (M_w/M_n) of obtained poly(ethylene) was to be 2.1–2.4, being consistent with the feature of polymers $(M_w/M_n = 1.9–2.5)$ produced with metallocene catalysts [4].

Fig. 3 shows the relationship between the catalytic activity per mmol of Ind_2ZrCl_2 and the amount (mg) of $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ with three different compositions, obtained at $[BuLi]/[MoS_2]$ ratios of 0.5, 0.8, and 2.0. The catalytic activity increased with increasing amount of $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ and is much higher for the $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ with high $Ph(Me)_2NH^+$ content (high z content) for the same amount of $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$. The relationship between the catalytic activity and the total $Ph(Me)_2NH^+$ content in the $[Ph(Me)_2NH^+]_z$ $[MoS_2]^{z-}$ cocatalyst is shown in Fig. 4. The catalytic

Table 4
Ethylene polymerization with N,N-dimethylanilinium ion intercalated MoS_2 at various feed ratios

Run no.	Ind_2ZrCl_2 (μmol)	$AlEt_3$ (μmol)	$[Ph(Me)_2NH^+]_{0.14}$ $[MoS_2]^{0.14-}$ (mg)	Ethylene pressure (MPa)	Activity (kg/(mmol Zr h))	$M_n \times 10^{-4}$	M_w/M_n
1	1	500	0	2.0	18	27	2.3
2	1	500	26	2.0	23	19	2.2
3	1	500	65	2.0	40	–	–
4	1	500	121	2.0	86	14	2.1
5	1	500	167	2.0	105	–	–
6	1	500	129	0.6	27	7	2.4

Polymerization conditions: toluene, $500\,ml$; polymerization temperature, $80\,^\circ C$; polymerization time, $60\,min$.
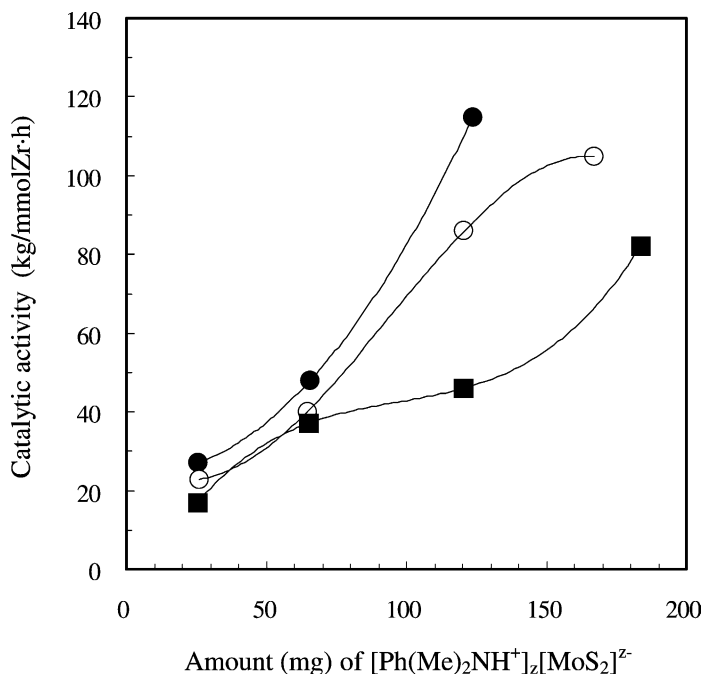
Fig. 3. Catalytic activity as a function of amount (mg) of $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ for the ethylene polymerization with Ind_2ZrCl_2/Et_3Al catalyst activated with $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ obtained at different $[BuLi]/[MoS_2]$ ratios of 2.0, 0.8, and 0.5: z, (●) 0.20, (○) 0.14, and (■) 0.09; Ind_2ZrCl_2, 1 μmol; Et_3Al, 500 μmol; toluene, 500 ml; ethylene pressure, 2.0 MPa; temperature, 80 °C; time, 60 min.

activity increases with the total $Ph(Me)_2NH^+$ content in the $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ cocatalyst regardless of the amount of $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$. This indicates that only the $Ph(Me)_2NH^+$ intercalated MoS_2 contributes effectively to the activation of $Ind_2ZrCl_2/AlEt_3$ catalyst and MoS_2 does not.

Ethylene polymerization was investigated by using $Ind_2ZrCl_2/AlEt_3$ catalyst activated with $[Ph(Me)_2 NH^+]_z[MoS_2]^{z-}$ having different composition, in which $Ph(Me)_2NH^+$ was intercalated in all interlayer space of MoS_2, obtained from different hydration conditions in Table 3. Fig. 5 shows the relationship between the catalytic activity and the total $Ph(Me)_2NH^+$ content in $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ cocatalyst. The catalytic activity increases with the increase in total $Ph(Me)_2NH^+$ content for the cocatalysts with $Ph(Me)_2NH^+$ of 0.17, 0.20, and 0.23 mol/mol of MoS_2 except for the $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ cocatalyst with $Ph(Me)_2NH^+$ of 0.12 mol/mol, where enhancement of the catalytic activity was hardly observed. The basal plane of MoS_2 crystal is composed

of a monolayer of sulfur atoms; however, the edge surface is composed of one-dimensionally (1D) arranged sulfur and molybdenum atoms. Accordingly, the isomerization reaction of olefins with MoS_2 as catalyst is reported to proceed only on the edge site of MoS_2 [19]. With respect to the crystal of $Ph(Me)_2NH^+$ intercalated MoS_2, $Ph(Me)_2NH^+$ are only on the edge site and not on the basal. Consequently, only the edge site is considered to act effectively for the activation of the metallocene catalysts. Probably, the slight enhancement is due to the decrease in the amount of $Ph(Me)_2NH^+$ present in the edge site of MoS_2. This indicates that more than 0.17 mol/mol of $Ph(Me)_2NH^+$ in the cocatalyst is needed for the activation of metallocene catalyst by addition of the $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ cocatalyst, where the $Ph(Me)_2NH^+$ was intercalated into all interlayer space of MoS_2.

It was found that the catalytic activity of the $Ph(Me)_2NH^+$ intercalated MoS_2 significantly depended upon the concentration of $Ph(Me)_2NH^+$
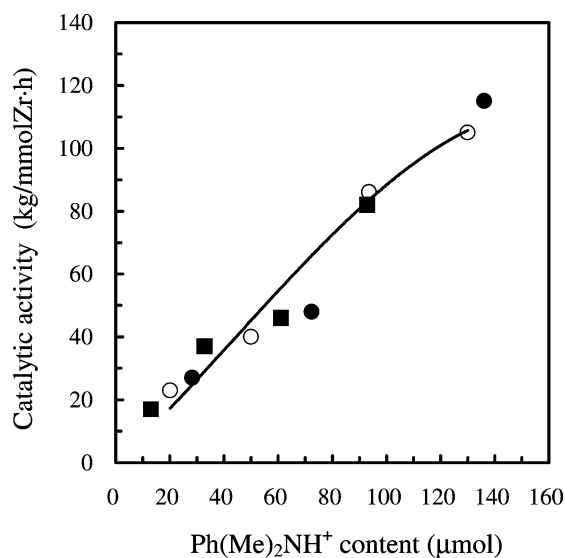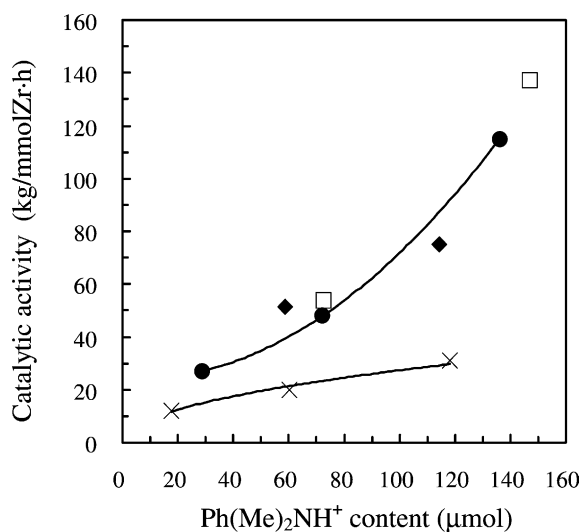
Fig. 4. Catalytic activity as a function of total $Ph(Me)_2NH^+$ content (μmol) in $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ cocatalyst for the ethylene polymerization with Ind_2ZrCl_2/Et_3Al catalyst activated with $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ obtained at different $[BuLi]/[MoS_2]$ ratios of 2.0, 0.8, and 0.5: z, (●) 0.20, (○) 0.14, and (■) 0.09; Ind_2ZrCl_2, 1 μmol; Et_3Al, 500 μmol; toluene, 500 ml; ethylene pressure, 2.0 MPa; temperature, 80 °C; time, 60 min.

Fig. 5. Catalytic activity as a function of total $Ph(Me)_2NH^+$ content (μmol) in $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ cocatalyst of the ethylene polymerization with the Ind_2ZrCl_2/Et_3Al catalyst in the presence of $[Ph(Me)_2NH^+]_z[MoS_2]^{z-}$ obtained under different hydration conditions and at the same $[BuLi]/[MoS_2]$ ratios of 2.0: z, (□) 0.23, (●) 0.20, (◆) 0.17, and (×) 0.12; Ind_2ZrCl_2, 1 μmol; Et_3Al, 500 μmol; toluene, 500 ml; ethylene pressure, 2.0 MPa; temperature, 80 °C; time, 60 min.

present in the interlayer spaces of MoS_2. Therefore, it is proposed that neutral dialkylmetallocene would be activated by the $Ph(Me)_2NH^+$ intercalated MoS_2 according to the mechanism as shown in Scheme 2 and transformed into catalytically active species.

The neutral dialkylmetallocene is protonated by the $Ph(Me)_2NH^+$ in the interlayer space of MoS_2, especially on the edges of layered structure of MoS_2,

to form the cationic monoalkylmetallocene as an active species with liberation of a neutral amine, *N,N*-dimethylaniline. Here, the two-dimensional (2D) macroanion of MoS_2 acts as a non-coordinating counter anion toward the formed cationic species and the catalytically active species exist in a salt form of the cationic metallocene species with the 2D macroanion of MoS_2.
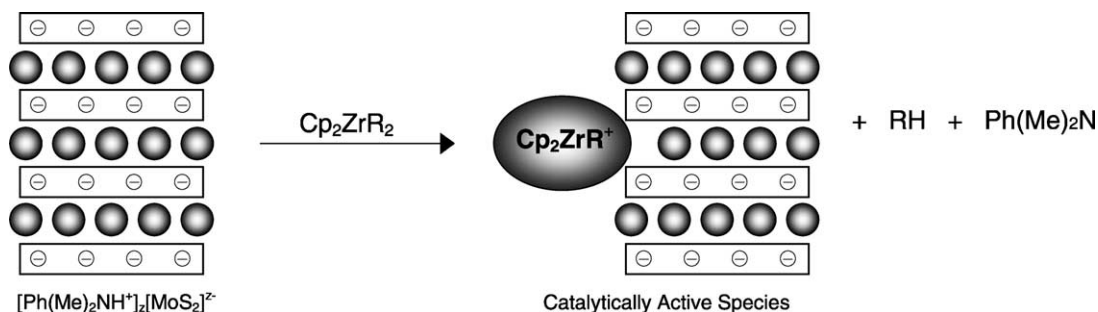
Scheme 2. Scheme for activation of metallocene catalyst with *N,N*-dimethylanilinium ion intercalated MoS_2.

Table 5
Ethylene/1-hexene copolymerization with the Ind_2ZrCl_2/Et_3Al catalysts activated with $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ and with $[Ph(Me)_2NH^+][B(C_6F_5)_4{}^-]$

Run no.	Ind_2ZrCl_2 (μmol)	$AlEt_3$ (μmol)	Cocatalyst		Activity	$M_n \times 10^{-4}$ (kg/(mmol Zr h))	M_w/M_n	T_m (°C)
1	3	500	$[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$	364 mg	16	4.6	2.3	129
2	2	2200	$[Ph(Me)_2NH^+][B(C_6F_5)_4{}^-]$	6 mmol	95	4.3	2.3	126

Polymerization conditions: *n*-hexane, 1200 ml; ethylene, 0.6 MPa; 1-hexene, 20 ml; polymerization temperature, 80 °C; polymerization time, 90 min.

3.3. Ethylene/1-hexene copolymerization with metallocene catalyst activated with N,N-dimethylanilinium ion intercalated MoS₂

Copolymerization of ethylene and 1-hexene was carried out with the Ind_2ZrCl_2/Et_3Al catalyst activated with $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ cocatalyst. The result is summarized in Table 5 together with that of the Ind_2ZrCl_2/Et_3Al catalyst activated with $[Ph(Me)_2NH^+][B(C_6F_5)_4{}^-]$. The catalytic activity per mmol of Ind_2ZrCl_2 in catalyst system activated with $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ was lower than that in catalyst activated with $[Ph(Me)_2NH^+][B(C_6F_5)_4{}^-]$. The copolymer obtained with the Ind_2ZrCl_2/Et_3Al catalyst activated with $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ had the molecular weight of 4.6×10^4 and a polydis-persity index (M_w/M_n) of 2.3, which were almost the same ($M_n = 4.3 \times 10^4$ and $M_w/M_n = 2.3$) as those for the copolymer obtained with the Ind_2ZrCl_2/Et_3Al catalyst activated with $[Ph(Me)_2NH^+][B(C_6F_5)_4{}^-]$. The CFC measurement was carried out to find the copolymer composition distribution; the CFC charts are shown in Fig. 6. Both the copolymers had a narrow chemical composition distribution. These results indicate that the ethylene/1-hexene copolymer (poly(ethylene-*co*-1-hexene)) obtained with the Ind_2ZrCl_2/Et_3Al catalyst activated with $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ cocatalyst has typical features of copolymers obtained with conventional metallocene catalysts, suggesting that the cationic monoalkylmetallocene as an active species have been supported structurally intact on the 2D macroanion of MoS_2.
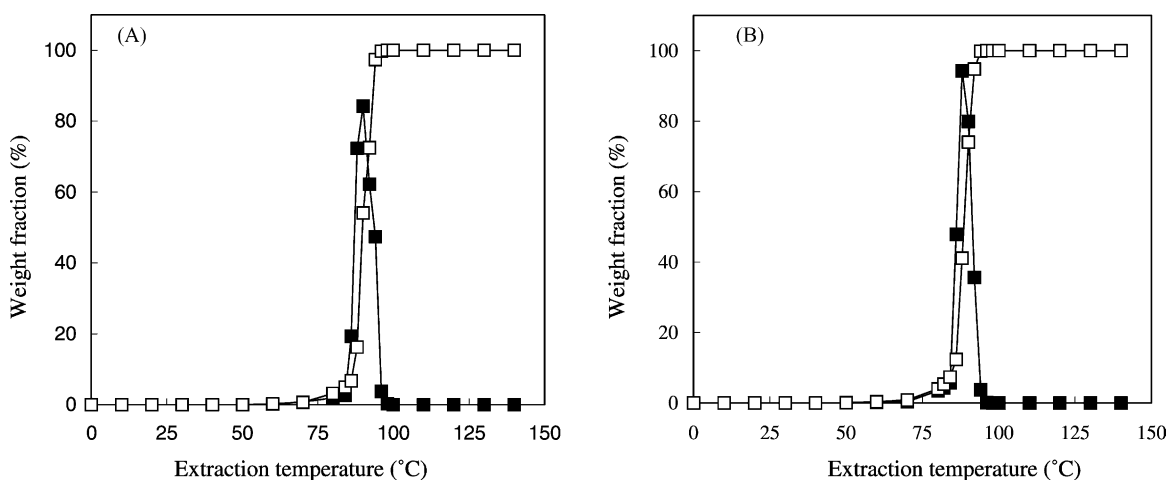

Fig. 6. The CFC curves of poly(ethylene-*co*-1-hexene) obtained with the $Ind_2ZrCl_2/AlEt_3$ catalyst activated with: (A) $[Ph(Me)_2NH^+]_{0.14}[MoS_2]^{0.14-}$ and (B) $[Ph(Me)_2NH^+][B(C_6F_5)_4{}^-]$; (□) integral lines and (■) differential lines.

4. Conclusions

The synthesis of $Ph(Me)_2NH^+$ salts of anion obtained by "topotactic" reduction of MoS_2 with BuLi, the effect of these compounds as a cocatalyst on the catalytic activity of Ind_2ZrCl_2/Et_3Al in ethylene polymerization, and the structure of poly(ethylene) and poly(ethylene-*co*-1-hexene) obtained with this catalyst system were investigated. Li^+ intercalated in interlayer space of MoS_2 by "topotactic" reduction of MoS_2 with BuLi is hydrated and then exchanged to $Ph(Me)_2NH^+$. In ethylene polymerization, addition of these $Ph(Me)_2NH^+$ salts to the Ind_2ZrCl_2/Et_3Al catalyst improves the catalytic activity per mmol of Ind_2ZrCl_2 and the catalytic activity increases with increasing amount of the cocatalyst. Poly(ethylene) and poly(ethylene-*co*-1-hexene) obtained with the metallocene activated by this cocatalyst have typical features such as narrow molecular weight distribution and narrow composition distribution like the polymers obtained with conventional metallocene catalysts. So, we propose that $Ph(Me)_2NH^+$ in the interlayer space of MoS_2, especially on the edges of layered structure of MoS_2 would activate neutral dialkylmetallocene into cationic monoalkylmetallocene by protonolysis. The 2D macroanions of MoS_2 would act as non-coordinating anions and supports for the obtained cationic species. We have no experimental evidence at present for this activation mechanism. If $Ph(Me)_2NH^+$ on the edge of layered structure of MoS_2 activate neutral metallocene, the catalytic activity would increase with the decrease in the crystallite size in the direction parallel to the basal plane of MoS_2. From such a viewpoint, a more detailed study is now being carried out, and the results will be published elsewhere.

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