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Zirconocene catalyst well spaced inside modified montmorillonite for ethylene polymerization: role of pretreatment and modification of montmorillonite in tailoring polymer properties

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Abstract

Zirconocene catalyst was heterogenized inside an organosilane-modified montmorillonite (MMT) pretreated by calcination and acidization, for supported catalyst systems with well-spaced α-olefin polymerization active centers. The varied pretreatment and modification conditions of montmorillonite are efficient for supported zirconocene catalysts in control of polyethylene microstructures, in particular, molecular weight distribution. In contrast to other supported catalyst systems, Cp_2ZrCl_2/modified montmorillonite(MMT-7)-supported catalysts with a distinct interlayer structure catalyzed ethylene homopolymerization and copolymerization with 1-octene activated by methylaluminoxane (MAO), resulting in polymers with a bimodal molecular weight distribution (MWD).

Keywords: Montmorillonite; Zirconocene; Polyethylene; Molecular weight; Molecular weight distribution; Chemical composition

1. Introduction

Metallocenes are generally single-site catalysts producing polymers of narrow molecular weight distribution (MWD) and chemical composition distribution [1–3]. It is possible to control polymer microstructures through catalyst design, although a correlation between catalyst structure and chain properties still needs to be better understood [4,5]. It is also possible to control polymer microstructures by mixing two single-site catalysts in a given polymerization [6,7]. Furthermore, many researchers are interested in obtaining bimodal polyethylenes using bicomponent catalysts or catalysts with special ligands or activators [8–10]. Polyethylene with a bimodal MWD from supported single-component metallocene catalysts however, has not been reported, because of different chemical or physical environments around active sites.

Layered silicates, in particular those with a 2:1 structure, exhibit a wide diversity of interaction reactions and also may themselves interact with the guest molecules [11–13]. Hydroxyl groups are the main surface constituents playing an important role in the intercalation of guest molecules [14–17], suggesting that guest molecules can be anchored at specific sites on the surface by specific reactions [18–20]. Several silica-supported metallocene catalyst systems have been reported [21,22]. They may be grouped into two types: MAO mediated [23,24] (in which the surface of silica is modified with MAO prior to metallocene impregnation) and directly supported [25,26]. These procedures afford different catalysts, which, in turn, produce polyolefins with different properties. Very recently, cuboctametric silsesquioxane mono(silanol), which is employed to mimic the surface of partially dehydroxylated silica, was used in modeling the surface reaction between metallocenes and silica [27]. So far, metallocene heterogenization studies indicate that physical impregnation onto or grinding with supports such as silica does not give rise to a catalyst system of practical application. This is due to a drastic reduction of catalyst activity, mainly attributed to the rather low quantities of metallocene immobilized [28–30]. Another reason might be the presence of the silica surface itself, which plays the role of a sterically demanding ligand close to the active site, therefore inhibiting monomer coordination. Finally, catalyst systems with higher metal contents achieved by chem-

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ical impregnation suffer from destruction of active sites from bimetallic interactions.

We chose to investigate the potential of using montmorillonite (MMT) as a support for neutral zirconocene in ethylene polymerization. Most of the studies employing chemically modified MMT concern improving monomer access to active sites through the use of a spacer between the silica surface and the metallocene species, and, as judged from reported catalyst activities, many have been quite successful [13,31–33]. These systems provide a way of modifying the activity and selectivity of these catalytically active centers by designing physical and chemical properties of host lattices. Thus, there is the potential of tailoring polymer properties.

2. Experimental

2.1. Materials

High-purity sodium montmorillonite was from Kunipia-F, Kunimine Co. (3-Aminopropyl)triethoxysilane (APTEOS) was purchased from Aldrich. Cp_2ZrCl_2 is a commercial product (Aldrich). Methylaluminoxane (MAO) in toluene (10 wt%) was from Ethyl Corp. Toluene (Analytical Reagents, Tianjing Reagents Factory) was dried over 4A molecular sieves for 10 days and then refluxed over Na/K alloy for 8 h. Polymerization grade ethylene (Liaoyang Chemical Corp.) was used without further treatment. 1-Octene (supplied by Liaoyang Chemical Corp.) was distilled under reduced pressure. Hydrochloric acid was of A.R. grade and used without further purification.

2.2. Preparation of APTEOS-modified montmorillonite

MMT was calcined above 500 °C for 5 h to get dehydroxylated montmorillonite (called MMT-1). Ten grams of MMT or MMT-1 was added into 250 mL of 6 N HCl in a 500 mL-three-necked flask and stirred vigorously at 80 °C for 12 h. The acidified MMT (called MMT-2) or acidified MMT-1 (called MMT-3) was filtered and dried at 120 °C under vacuum for 24 h. And then 5 g of MMT or MMT-1 or MMT-2 or MMT-3 was refluxed with 5 mL of APTEOS in 100 mL of toluene at 70 °C for 24 h. The resulting APTEOS-modified MMT, MMT-1, MMT-2, and MMT-3 (called MMT-4, MMT-5, MMT-6, and MMT-7, respectively) were filtered and dried at 80 °C under vacuum for 24 h.

2.3. Preparation of supported catalysts

The mixture of 1 g APTEOS-modified montmorillonite (MMT-4, MMT-5, MMT-6, and MMT-7) and 20 mmol MAO in 50 mL of toluene was stirred at 50 °C for 5 h. The liquid phase was leached, and then 0.4 mmol of zirconocene Cp_2ZrCl_2 in 50 mL of toluene was added and the mixture was stirred at 50 °C for 24 h. The final solids were collected by filtration, washed with toluene, and dried under vacuum at 40 °C for 24 h to give Cp_2ZrCl_2/MAO/MMT-4 (Cp_2ZrCl_2/MAO/MMT-5, Cp_2ZrCl_2/MAO/MMT-6, or Cp_2ZrCl_2/MAO/MMT-7). On the other hand, 1.00 g of APTEOS-modified montmorillonite was directly reacted with 0.4 mmol of zirconocene Cp_2ZrCl_2 in 50 mL of toluene at 50 °C for 24 h to give Cp_2ZrCl_2/MMT-4, Cp_2ZrCl_2/MMT-5, Cp_2ZrCl_2/MMT-6, and Cp_2ZrCl_2/MMT-7, respectively. All operations were performed under nitrogen atmosphere.

2.4. Polymerization

Ethylene polymerization was carried out under stirring in a 200-mL Schlenk-type reactor. After the reactor was heated and evacuated for about 30 min, ethylene (and comonomer), toluene, and a calculated amount of the cocatalyst MAO were put in succession into the reactor. Polymerization started with the addition of the catalyst. After polymerization for 0.5 h at 25 °C, an acidified ethanol solution was quickly injected to terminate the polymerization. The precipitated polymer was collected, washed several times with ethanol, and dried at 40 °C under vacuum for 24 h.

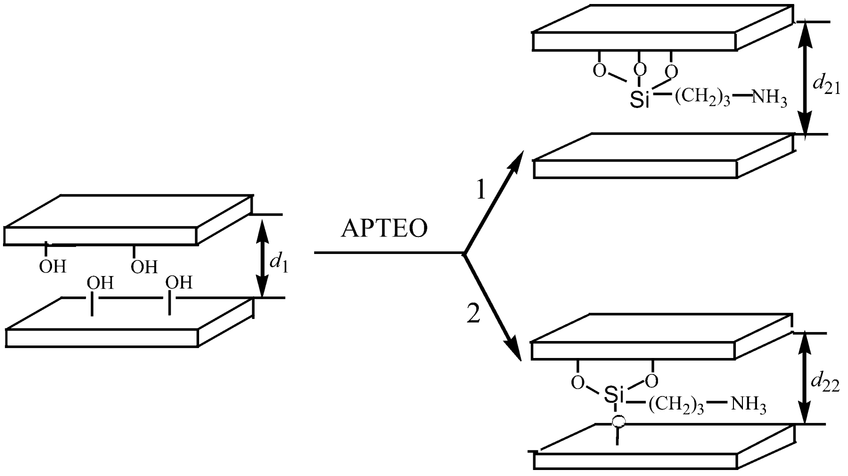
2.5. Characterization

The interlayer spacings of MMT, MMT-4, MMT-5, MMT-6, MMT-7, and their corresponding supported catalyst were determined by X-ray diffraction with a Rigaku Dlmax-IIB X-ray diffractometer (XRD) with Cu-K_α radiation. The accelerating voltage was 40 kV, and the current was 20 mA. Zr contents of the supported catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with Plasma-Dec (I) of America Leeman Lab. Possible reactions in the preparation of the supported catalysts were also examined by X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded on a VG Escalab MK II spectrometer using an Al-K_α exciting radiation from an X-ray source operated at 10.0 kV and 10 mA. Molecular weights and molecular weight distribution of the polymers were determined by gel-permeation chromatography (GPC) on a Waters 150C using 1,2,4-trichlorobenzene as solvent at 150 °C. A differential scanning calorimetry (DSC) DSC-7 instrument was used in measuring the melting temperature (T_m) of the polymers at a heating rate of 10 °C/min from 20 to 200 °C under nitrogen atmosphere. ^{13}C NMR spectra of the copolymers were recorded at 120 °C on a Varian Gemini 2000 NMR spectrometer operating at 400 MHz, with a 6-s delay, analyzed by the method of Kimura et al. [34].

3. Results and discussion

3.1. Preparation of supports

So far, MMT sustained a single interlayer spacing structure with only a change of interlayer spacing when modified



Scheme 1. Schematic presentation of modification of MMT.

by organic guests. Unexpectedly, the modified montmorillonite MMT-7 has two distinct interlayer spacings ($d_{11} = 2.08$ nm; $d_{12} = 1.10$ nm) (Fig. 1, e), which is different from other modified MMTs with only a single interlayer spacing (MMT-4, $d_1 = 1.16$ nm; MMT-5, $d_1 = 1.27$ nm; and MMT-6, $d_1 = 1.32$ nm) (Fig. 1, b–d), though they were derived from the same MMT with a single interlayer spacing ($d_1 = 0.96$ nm) (Fig. 1, a). This shows that there are different reaction modes between APTEOS and pretreated MMT in the preparation of modified MMT. Undoubtedly, the difference results from the different pretreatments and modification of MMT. The surface chemistry of MMT had been dehydroxylation taking place between silanol groups lying in the same wafers of clay microcrystals. The surface density of silanol groups on fully hydroxylated silica is about 4.9 nm^{-2}, regardless of the type of silica, but thermal treatment at 723 K reduces this number to about 1.2–1.5 nm^{-2} by silanol condensation. Silanol groups are capable of reacting with agents such as organometallic chlorides and alkoxydes. In the present case, APTEOS can react either with OH functionalities lying in the same surface of MMT (reaction 1) or with those lying in surfaces of adjacent platelets of MMT (reaction 2) (Scheme 1), depending upon the surface density of OH functionalities or the possible existence of different kinds of OH sites because of pretreatment of the support [35]. The different reaction modes result in MMT-7 with two distinct interlayer spacings ($d_{11} = 2.08$ nm and $d_{12} = 1.10$ nm). It is not known in what proportion these two types of –O–Si–O– links are. It is imagined that even only one or more cross-surface links would pull the interlayers closer, which would facilitate further gap-filling crosslinks and shorten the interlayer spacings. This dual mode of –O–Si–O– linkage is interesting in that the different interlayer spacings result in a bimodal molecular weight distribution of the polymers as noted below. Additionally, there probably existed only one of two reaction modes or all two reaction modes in the same lattice in the preparation of the modified MMTs with a single interlayer spacing. So the pretreatment of MMT has a significant influence on the interlayer structures of the resulting modified MMTs. This will further affect the anchorage of coming zirconocene compounds.

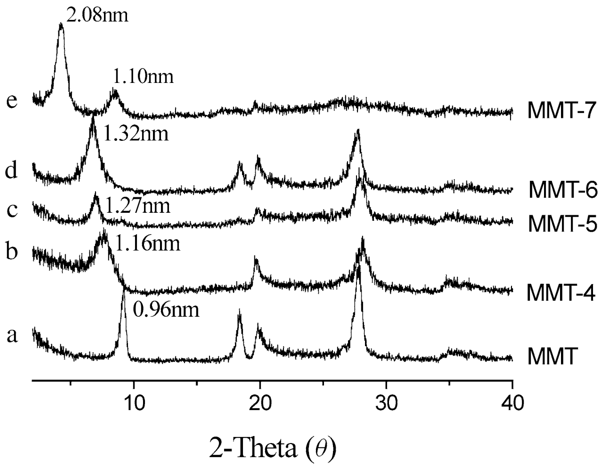


Fig. 1. XRD spectra of montmorillonite (MMT) and (3-aminopropyl)-triethoxysilane (APTEOS)-modified montmorillonites (MMT-4, -5, -6, and -7).

3.2. Preparation of supported catalysts

For the supported catalysts, the MMT-7-supported catalyst without MAO (Cp_2ZrCl_2/MMT-7) still inherited an interlayer structural characteristic with two separate larger interlayer spacings ($d_{21} = 2.45$ nm; $d_{22} = 1.33$ nm) (Fig. 2, d), but the MMT-7-supported catalyst with addition of MAO (Cp_2ZrCl_2/MAO/MMT-7) possessed only a single larger interlayer spacing ($d_2 = 2.22$ nm) (Fig. 2, h), compared to the support MMT-7 with two distinct interlayer spacings ($d_{11} = 2.08$ nm; $d_{12} = 1.10$ nm) (Fig. 1, e). So the addition of MAO destroyed the original interlayer structure of MMT-7. On the other hand, other supported catalysts whether with or without the addition of MAO, however, still kept single larger interlayer spacings (Fig. 2, a–c and e–g), compared to their corresponding supports with single interlayer spacings (Fig. 1, b–d).

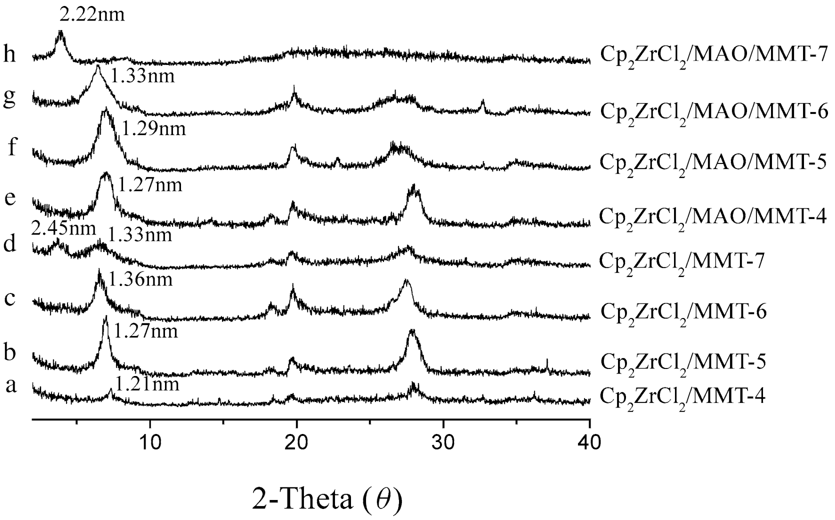


Fig. 2. XRD spectra of APTEOS-modified montmorillonite-supported Cp_2ZrCl_2 catalysts.

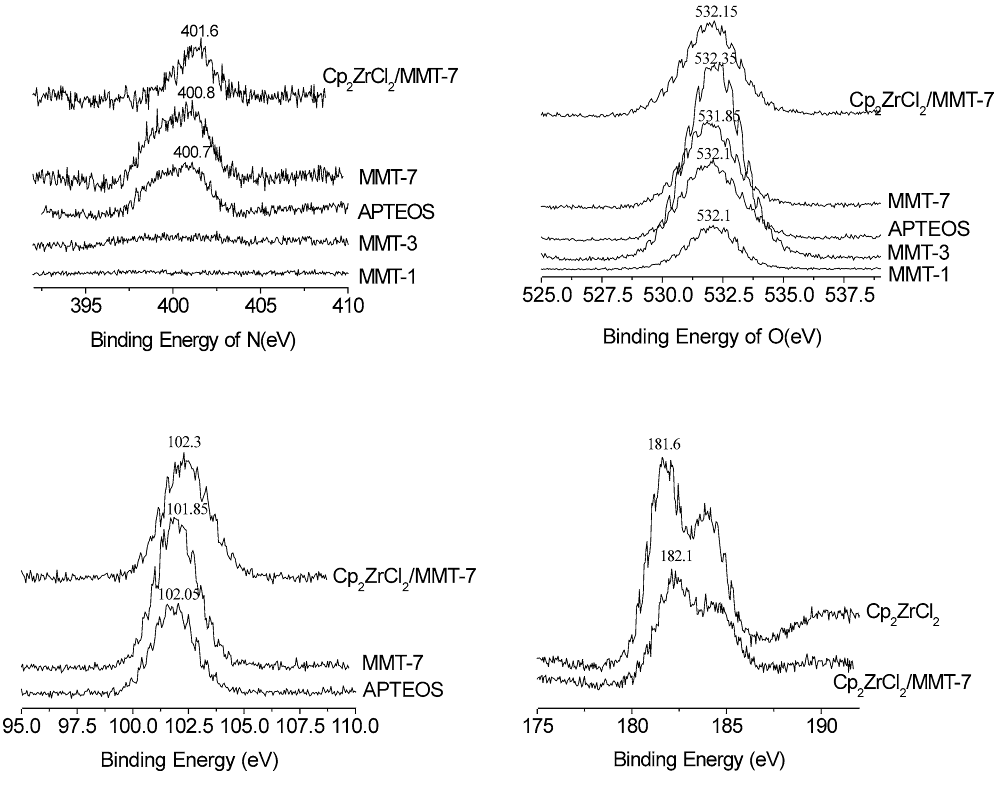


Fig. 3. XPS spectra of montmorillonite (MMT), modified MMT, and supported catalyst.

XPS spectra were used to investigate the changes of binding energy of reactive atoms in the formation of the supported catalyst Cp_2ZrCl_2/MMT-7 (Fig. 3). The following changes in the XPS spectrum were observed: a rise of 0.8 eV in the binding energy of N of the supported catalyst over that of MMT-7, a rise of 0.5 eV in the binding energy of Zr of the supported catalyst over that of Cp_2ZrCl_2, a rise of 0.45 eV in the binding energy of Si of the supported catalyst over that of MMT-7, and a drop of 0.2 eV in the binding energy of O of the supported catalyst than that of MMT-7. These imply strong interactions between MMT-7 and zirconocene immobilized in the galleries of the MMT. It is also proved by the high Zr loading as noted below.

The Zr loadings of the supported catalysts without MAO are much higher than those with MAO (Table 1, entries $1 > 5$, $2 > 6$, $3 > 7$, $4 > 8$). As we well know, MAO can reduce the number of OH groups on the surface of silica, resulting in a decrease of generating mono- (Scheme 2, I) or bidentate (Scheme 2, II) surface species, which results in a decrease of Zr loading. Additionally, different pretreatments

Table 1
Results of the catalysts preparation and their performance in ethylene homopolymerization

Entry	Supported catalysts[a]	d_1[b] (nm)	d_2[c] (nm)	Zr loading (mg_{Zr}/g_{cat})	Activity ($kg_{PE}/(mol_{Zr}$ h))[d]	M_w[e] ($\times 10^{-4}$)	MWD[e]	T_m[f]
1	Cp_2ZrCl_2/MMT-4	1.16	1.21	36.8	2820	10.58	3.19	123.6
2	Cp_2ZrCl_2/MMT-5	1.27	1.27	31.4	569	15.88	3.61	126.9
3	Cp_2ZrCl_2/MMT-6	1.32	1.36	16.8	1192	12.77	2.29	124.2
4	Cp_2ZrCl_2/MMT-7	1.10 and 2.08	1.33 and 2.45	28.1	2630	6.57	6.06	111.4
5	Cp_2ZrCl_2/MAO/MMT-4	1.16	1.27	11.2	2108	11.17	2.76	125.7
6	Cp_2ZrCl_2/MAO/MMT-5	1.27	1.29	24.7	1283	11.91	2.66	124.8
7	Cp_2ZrCl_2/MAO/MMT-6	1.32	1.33	5.87	1017	11.24	2.28	122.7
8	Cp_2ZrCl_2/MAO/MMT-7	1.10 and 2.08	2.22	3.9	1206	8.87	2.83	124.9

[a] The preparation of catalysts (entries 1–4): 1 g support was directly mixed with 0.4 mmol Cp_2ZrCl_2 in 50 mL toluene at 50 °C for 24 h. The preparation of catalysts (entries 5–8): after 1 g support was stirred with 20 mmol MAO in 50 mL toluene at 50 °C for 5 h, 0.4 mmol Cp_2ZrCl_2 in 50 mL toluene was added with stirring at 50 °C for 24 h.

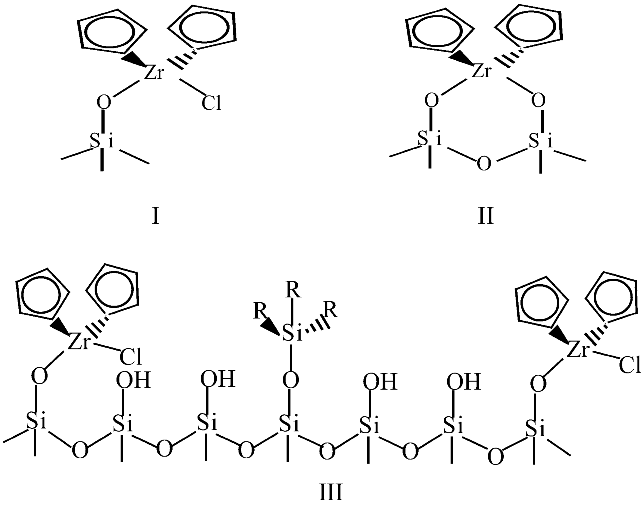
[b] The interlayer spacing of supports (APTEOS-modified MMT) measured by XRD.

[c] The interlayer spacing of supported catalysts measured by XRD.

[d] Polymerization conditions: Zr = 2.5 μmol, Al/Zr total molar ratio = 800, $T = 25\,°C$, $t = 30$ min, $P_{C_2H_4} = 1$ atm in 100 mL toluene.

[e] Molecular weight and molecular weight distribution determined by GPC.

[f] Melting temperature of polymer determined by DSC.



Scheme 2. The surface species of modified MMT supported zirconocene catalyst.

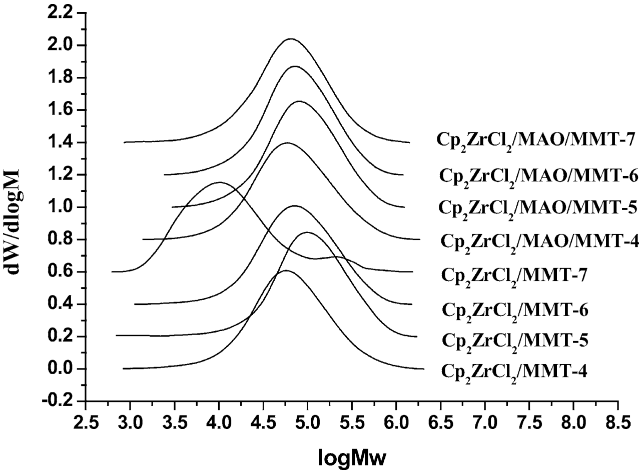


Fig. 4. Effect of the supports and MAO treatments on GPC curves of polyethylenes from the supported catalysts.

of MMT (including dehydroxylation and acidification) result in different Zr loadings. The acidification of MMT partly decreases the Zr loadings (Table 1, entries 3 < 1, 4 < 2, 7 < 5, 8 < 6). The dehydroxylation of MMT has a different influence because of different treatments. It is generally difficult to compare the chemical behavior as in a homologue series due to the diversity in the distribution and content of reactive functionalities in the galleries of MMT. However, gross examination of the pretreatments affords insight into their general response to catalyst preparation and polymerization conditions, paving the road for further studies.

3.3. (Co)polymerization of ethylene and characterization of the polymers

All the supported catalysts were evaluated in ethylene homopolymerization (Table 1). All the supported catalysts, in particular Cp_2ZrCp_2/MMT-4, Cp_2ZrCp_2/MMT-7, and Cp_2ZrCp_2/MAO/MMT-4, show high catalytic activity, except that Cp_2ZrCp_2/MMT-5 shows mild activity. High catalyst loading does not mean high catalyst activity, because there possibly exists deactive bidentate surface species (Scheme 2, II) or deactivation occurring through a bimolecular reaction between neighboring centers, which should be avoidable by spacing such catalyst species (Scheme 2, III) on the silica surface. We can also see that the use of MAO in the preparation of supported catalysts does not always increase the catalytic activity (entries 5 < 1, 7 < 3, 8 < 4). So it is claimed that additional MAO is not always necessary during the preparation of supported catalysts, and whether it necessary or not is determined by the nature of the supports. Unexpectedly, the polyethylene catalyzed by Cp_2ZrCp_2/MMT-7 catalyst is bimodal in molecular weight distribution, but has a lower MW and a broader MWD than those catalyzed by other supported catalysts (Fig. 4). But the melt temperature (T_m) of the polymer in the former case is

Table 2
Results of ethylene (co)polymerization with the supported catalyst Cp_2ZrCl_2/MMT-7[a]

Entry	1-Octene (mL)	Al/Zr (molar ratio)	Activity (kg_{PE}/ (mol_{Zr} h))	M_w[b] ($\times 10^{-4}$)	MWD[b]	1-Octene content[c] (mol%)	T_m[d] (°C)
1		500	1147	8.84	6.87		125.1
2		1000	1891	8.82	6.56		124.4
3		1500	1097	7.01	5.77		122.7
4[e]		1000	739	23.1	2.44		124.4
5	2	500	1799	5.86	4.80	3.63	117.3
6	2	1000	2246	6.57	6.06	3.14	111.4
7	2	1500	1535	5.75	4.73	3.50	114.9
8	5	1000	1695	5.71	4.06	8.00	102.1
9[e]	2	1000	902	10.00	2.60	1.23	115.0
10[e]	5	1000	601	6.39	2.95	3.47	108.9

[a] General polymerization conditions: Zr = 2.5 µmol, $T = 25\,°C$, $t =$ 30 min, $P_{C_2H_4} = 1$ atm, in 100 mL toluene.

[b] Molecular weight and molecular weight distribution determined by GPC.

[c] 1-Octene contents in copolymers determined by ^{13}C NMR.

[d] Melting temperature of polymer determined by DSC.

[e] Homogeneous Cp_2ZrCl_2/MAO catalyst.

lower than those of the polymers in the latter cases, depending upon their MWs.

Cp_2ZrCl_2/MMT-7 catalyst was further evaluated in ethylene homo- and copolymerization with 1-octene (Table 2). Different amounts of the cocatalyst MAO and comonomer 1-octene resulted in a different polymerization behavior in ethylene (co)polymerization. The supported catalyst had much higher catalytic activities in ethylene homopolymerization (entries 1–3) and copolymerization (entries 5–8) than homogeneous Cp_2ZrCl_2/MAO catalyst (entries 4, 9, 10). For the supported catalyst, higher a Al/Zr molar ratio does not necessarily give higher catalytic activity in ethylene homopolymerization or copolymerization with 1-octene (see entries 1–3 and 5–7). There is an optimum concentration of MAO for the highest activity, because excess MAO results in a lower activity due to chain transfer and hindering the entrance of the monomers. On the other hand, activities of the supported catalyst in ethylene/1-octene copolymerization under a proper 1-octene concentration (entries 5–7) are higher than in ethylene homopolymerization (entries 1–3) at corresponding Al/Zr molar ratios. This is in accord with the generally known fact that a proper amount of α-olefin always enhances the rate of ethylene polymerization [36] as explained by the unstable diffusion hypothesis [37]. Excess long-chain 1-octene, however, slows down the tempo of monomer diffusion and partly annihilates the active species, resulting in a decrease in catalytic activity (entry 8).

Changes in MW and MWD of the resulting polymers are observed besides variation in polymerization activity with amount of cocatalyst and the comonomer. Under the same polymerization conditions, PEs produced by the supported catalyst have lower average MW and broader MWD than those by homogeneous catalyst. The average MW and melting temperature (T_m) of the polymers produced in ethylene homopolymerizations (entries 1–3) are higher than those in copolymerizations (entries 5–8).

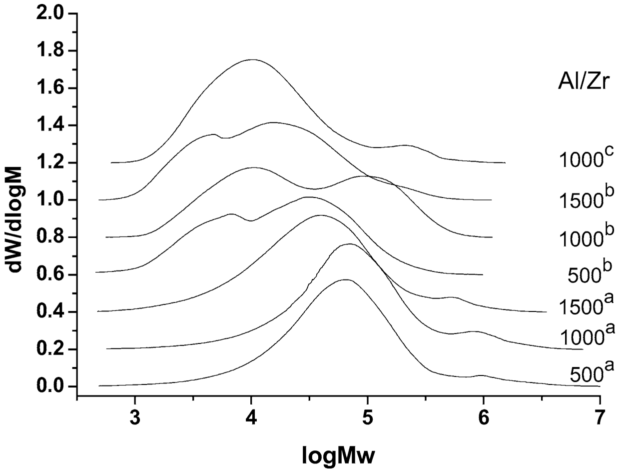


Fig. 5. Effects of Al/Zr molar ratios and content of 1-octene on GPC curves of homopolymers and copolymers of polyethylene produced with Cp_2ZrCl_2/MMT-7-supported catalyst (content of 1-octene: a, 0 mL; b, 2 mL; c, 5 mL).

In ethylene homopolymerization, an increase in Al/Zr ratio from 500 to 1000 brings about little changes in the average MW and MWD of the resulting polymers (entries 1 and 2), but the average MW of the PE decreased and the MWD of PE was narrower when the Al/Zr ratio was up to 1500 (entry 3). Obviously, the excess MAO accelerated chain transfer reactions [38]. In contrast, T_ms of PEs changed only little with variation in the Al/Zr molar ratio (entries 1–3), and the low-MW portion of PEs predominates and stays in relatively constant proportion (Fig. 5), the two different active species being in balance during homopolymerization.

In ethylene copolymerization, the concentrations of 1-octene and MAO have important effects on the properties of the resulting polymers. In the presence of 2 mL of 1-octene, the average MW of the copolymer produced at a Al/Zr molar ratio of 1000 (entry 6) is higher than that produced at Al/Zr molar ratios of 500 and 1500 (entries 5 and 7), with a broader MWD. As shown in GPC profiles (Fig. 5), the proportion of the high-MW portion of PE under a Al/Zr ratio of 1000 (entry 6) is higher than those under Al/Zr ratios of 500 and 1500 (entries 5 and 7). Variation in MWD with Al/Zr ratio, however, is difficult to interpret. The 1-octene content and T_m of the copolymers are almost invariant, probably due to the same concentration of 1-octene in the polymerization (entries 5, 6, and 7). However, upon increasing the concentration of 1-octene to 5 mL (entry 8), the average MW, MWD, and T_m of the copolymer under a Al/Zr ratio of 1000 decreased respectively than at an 1-octene content at 2 mL, showing that excess of long alkyl chain 1-octene hindered ethylene entrance at the active sites.

Expectedly, the MWD of all the PEs produced with the Cp_2ZrCl_2/MMT-7 catalyst is bimodal and the M_w/M_n values of all the PEs are over 4. According to Schulz–Flory's

Table 3
^{13}C NMR analysis of ethylene/1-octene copolymers[a]

Entry[b]	Sequence–length distribution									Number–average distribution[c]		[O][d] (mol%)	N[e]	$r_E\, r_O$[f]
	EE	EO+OE	OO	EEE	EEO+OEE	EOE	OEO	EOO	OOO	n_E	n_O			
5	0.9415	0.0585	0.0000	0.8762	0.0833	0.0198	0.0043	0.0129	0.0035	20.97	0.79	3.63	20.15	12.3
6	0.9248	0.0752	0.0000	0.8837	0.0849	0.0213	0.0000	0.0101	0.0000	22.82	0.74	3.14	11.93	7.67
7	0.9304	0.0696	0.0000	0.8685	0.0915	0.0220	0.0047	0.0099	0.0034	19.12	0.70	3.50	21.34	8.83
8	0.8568	0.1432	0.0000	0.7206	0.1917	0.0555	0.0069	0.0220	0.0033	8.94	0.79	8.00	56.36	2.67
9	0.9391	0.0609	0.0000	0.9486	0.0391	0.0123	0.0000	0.0000	0.0000	50.52	0.63	1.23	9.90	0.00
10	0.9278	0.0722	0.0000	0.8644	0.1007	0.0259	0.0000	0.0090	0.0000	19.17	0.69	3.47	23.90	5.06

[a] Analyzed by the method of Kimura; E, ethylene, O, 1-octene.

[b] Numbers correspond to entries in Table 2.

[c] According to the analysis of triad distribution.

[d] 1-Octene content in copolymers.

[e] Number of branch per 1000 carbon atoms.

[f] Reactivity ratio of monomer analyzed by the method of Carman: $r_E\, r_O = 1 + f(x+1) - (1+f)(1+x)^{1/2}$, where $f = n_E/n_O$, $x = (\mathrm{OOO}+\mathrm{OOE})/\mathrm{EOE}$.

statistical theory of polymers [39], there are at least two different kinds of active species when the M_w/M_n of a polymer is over 2. The M_w/M_n values of the resulting polymers are over 4, so there are at least two different kinds of active species, in agreement with the bimodal MWD in GPC profiles. A reasonable explanation of the bimodal MWD is the different spatial environments of the catalytic sites, due to two separate interlayer spacings of the Cp_2ZrCl_2/MMT-7 catalyst.

The microstructures of the copolymers were calculated from the ^{13}C NMR spectra (Table 3). EE diad of the copolymers produced with the supported catalyst in the presence of 2 mL of 1-octene at different Al/Zr molar ratios (entries 5–7) indicated that Al/Zr molar ratios have no obvious effect on the distribution of EE diad, close to copolymer polymerized by homogeneous catalysts (entries 9 and 10). On the contrary, EE diad for the product from the supported catalyst is lower than that of homogeneous catalyst with an increase in the content of 1-octene (entries 8 and 10). The EO + OE diads of the copolymer produced with the supported catalyst increased nearly two times when increasing 1-octene from 2 mL (entry 6) to 5 mL (entry 8), and higher than those of the copolymer produced with homogeneous catalyst under corresponding polymerization conditions (entry 6 vs entry 9, entry 8 vs entry 10). Triad EEE has a similar distribution tendency as the diad EE. However, the triads of EEO + OEE, EOE, EOO + OOE, and OOO of copolymers polymerized with the supported catalyst were much enhanced relative to that of homogeneous catalyst polymers. This means that the supported catalyst has a tendency to build up the 1-octene insertion in the copolymer, which was not shown in the case of homogeneous catalyst. The reactivity ratios of monomers ($r_E\, r_O$) during the copolymerization in the presence of 2 mL of 1-octene polymerized by the supported catalyst were larger than that by the homogeneous catalyst. This shows a stronger tendency of block copolymerization by the supported catalyst than by the homogeneous catalyst. However, upon increasing 1-octene up to 5 mL, the $r_E\, r_O$ value decreased on a large scale relative to that in presence of 2 mL of 1-octene. So the excess 1-octene is not available for the block copolymerization polymerized by the supported catalyst. The results show that 1-octene insertion branching is more favorable for the Cp_2ZrCl_2 confined inside the galleries of the modified MMT with different interlayer spacings than for the homogeneous catalyst.

4. Conclusions

The single-component Cp_2ZrCl_2 catalyst supported on the MMT modified by (3-aminopropyl)triethoxysilane was used for ethylene polymerization. Different pretreatments and modification of MMT and preparation modes of supported catalysts resulted in different ethylene polymerization behavior and polymers with different properties. Surprisingly, the resulting (co)polymers from Cp_2ZrCp_2/MMT-7 catalysts are bimodal in MWD due to differences in the chemical and physical environment of specific catalytic sites. So, not only catalysts with bicomponents or special activators or of special ligands but also single-component catalysts in diverse spatial environment can generate polymers with bimodal MWD. These interesting results should be taken into account when chemical composition distributions are customized with supported single-component zirconocene catalysts. This develops a new idea of designing preparation modes of supported single-component catalysts for ethylene polymerization to produce polymer resins with controlled molecular weight and molecular weight distribution, giving the potential special materials with the demanded properties. There is a very strong industrial push to generate supported olefin polymerization catalysts that yield polymers of controlled properties.

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