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Ethylene Homopolymerization and Ethylene/α-olefin Copolymerization Catalyzed by Supported Metallocene Catalysts with Boron Activators

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Abstract: In this paper, the supported metallocene catalysts were prepared, in which SiO_2 was used as the carrier, Cp_2ZrCl_2 was used as the main catalyst and MAO, $B(C_6F_5)_3$, $[HNMe_2Ph][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$, $B(C_6F_5)_3$/TMA were used as the activators respectively. The effect of the activators on the catalytic properties in ethylene homopolymerization and ethylene/α-olefins copolymerization was investigated. From the results, it was found that when the added amount of boron was 5.1×10^{-4} mol/g SiO_2, the molar ratio of B : Zr was between 14.10 ~ 19.04, the activity of the supported metallocene catalysts reached up to 10^7 g/(molZr · h) which was 511 ~ 1 090 times higher than that of MAO under the same conditions. The added amount of boron was only 1/16 of MAO for the same catalytic activity of 10^7 g/(molZr · h). Compared with the supported catalyst with $B(C_6F_5)_3$ as activator, the catalytic activity of supported metallocene catalyst with $[HNMe_2Ph][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ as activator was higher. It was also found that $[Ph_3C][B(C_6F_5)_4]$ system had the most narrow molecular weight distribution (MWD) and maximum 1-hexene content (2.97%). Copolymers prepared by the supported metallocene catalysts with boron activators had narrow MWD and density between 0.91 ~ 0.92 g/cm^3 which belonged to the scope of mLLDPE.

Key words: supported metallocene catalyst; boron; ethylene; α-olefin; copolymerization

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Metallocene catalysts provide higher activity and narrower molecular weight distribution (MWD) when compared with the conventional Ziegler-Natta catalysts.[1-2] However, it was found that the homogeneous metallocene catalytic systems have some disadvantages. Some advantages of using heterogeneous metallocene systems over their homogeneous counterparts are avoiding the bimolecular deactivation and β-H elimination, reduced need of aluminoxane compounds, avoiding the "fouling-effect", easy adaptation to use in the existing industrial polymerization processes, such as gas phase and slurry polymerization, good controllable morphology and high bulk density of polymer products[3-4]. Metallocene/SiO_2/MAO system[5] has been mostly used as supported metallocene catalyst, however, this system has some disadvantages. First of all, MAO has to be used in a very large stoichiometric excess in order to get high productivity catalysts. Secondly, MAO is a mixture of a variety of molecules. Furthermore, MAO is pyrophoric and reacts with water and air violently due to the high content of aluminum-carbon bonds. Actually, only one equivalent of boron activator with a well-defined structure is needed in order to obtain the same activity as MAO activator. And the synthesis of boron compound is rather security[3-4, 6-10]. Hlatky and coworkers[11-12] investigated the supported metallocene

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catalyst $[Cp_2ZrMe]^+[B(C_6F_5)_4\text{-}SiO_2]^-$. The result indicated that the catalyst system presented very high activity. Marks[13] and Ewen[14] used $B(C_6F_5)_3$ and alkyl metallocenes for olefin polymerization which also presented high activity. Tian Jun et al.[15] studied the functionalization of $B(C_6F_5)_3$ on partially hydroxylated silica and fully hydroxylated alumina and found that the Cp_2ZrMe_2/carrier/$B(C_6F_5)_3$ catalyst systems were active for olefin polymerization with a small amount of MAO and the polymer properties is similar to that of homogeneous system. However, the synthesis of alkyl metallocenes is difficult and very sensitive to air and moisture, so in this paper, Cp_2ZrCl_2 was used as the main catalyst. On the other hand, $B(C_6F_5)_3$ will be very easily eluted from the support material when washing with toluene during the preparation, which is due to the binding of $B(C_6F_5)_3$ to the surface hydroxyl groups is reversible, and so in this paper, $[HNMe_2Ph][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ was used as the activator in the preparation of the supported metallocene catalysts which were used for ethylene homopolymerization and ethylene/α-olefins copolymerization.

1 Experimental

1.1 Materials

All chemicals and polymerization were manipulated under argon atmosphere, using a glove-box and/or Schlenk techniques. Toluene was distilled over sodium/benzophenone before use. Silica gel (Lanzhou Chemical Engineering Research Center, PetroChina Company Limited) had a surface area of 322 m^2/g, a particle size of 55 μm and a bulk density of 0.28 g/cm^3. Trialkylaluminium (TMA, 2 mol/L in toluene) was purchased from Shangyu Hualun chemical Co., Ltd. Methylaluminoxane (MAO, 1.2 mol/L in toluene) was obtained from Lanzhou Chemical Engineering Research Center, PetroChina Company Limited. Tris (pentafluorophenyl) borane ($B(C_6F_5)_3$) was purchased from SPC scientific. Dimethylanilinium tetrakis(pentafluorophenyl) borate ($[HNMe_2Ph][B(C_6F_5)_4]$, 98%) and triphenylmethylcarbenium tetrakis (pentafluorophenyl) borate ($[Ph_3C][B(C_6F_5)_4]$, 97%) were purchased from J&K Scientific Ltd. 1-hexene (98%, Daqing Chemical Engineering Research Center, Institute of Petrochemical Engineering, PetroChina Company Limited) and 1-octene (98%, Tianjin Haina international trading Co., Ltd.) were out gassed by bubbling with N_2 and stored over 0.3 nm molecular sieves before use. Ethylene gas (99.9%, Chunyu special gases (Shanghai) Co., Ltd.) were dried by passing through a column of an oxygen-moisture trap. Bis(cyclopentadiene) zirconium dichloride (Cp_2ZrCl_2) was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd.

1.2 Catalyst Preparation

Support Treatment

To prepare the partially hydroxylated silica, silica gel support was packed into a horizontal quartz tube and calcined at 200 ℃ for 2 h and 600 ℃ for 4 h. After 6 h, the temperature was decreased to 25 ℃ with N_2 flow, and the silica powder was stored under vacuum until use.

The treated silica gel (2 g), MAO (16.4 mmol) or MAO (1.02 mmol) or $B(C_6F_5)_3$ (1.02 mmol) or $[HNMe_2Ph][B(C_6F_5)_4]$ (1.02 mmol) or $[Ph_3C][B(C_6F_5)_4]$ (1.02 mmol) or $Al(C_6F_5)_3$[16] (TMA 1.02 mmol and $B(C_6F_5)_3$ 1.02 mmol) and toluene (20 mL) were mixed together into a 100 mL of volumetric flask and refluxed for 2 h. Afterwards, the solids in the mixture were allowed to precipitate before collecting only the solid part with a medium fritted funnel and washing with toluene (2×10 mL). The product was dried under vacuum for 4 h.

Preparation of supported Catalyst

The desired amount of treated silica gel, Cp_2ZrCl_2 (0.44 mmol) and toluene (20 mL) were mixed together into a 100 mL of volumetric flask. After stirring vigorously for 2 h at 40 ℃. The solid part was collected with a medium fritted flask. The product was washed with toluene (3×10 mL) and then dried under vacuum for 4 h.

1.3 Polymerization

The ethylene polymerization was carried out in a 1 L stainless steel reactor (Pressure Product Industrial) equipped with a magnetic stirrer and Teflon liner. The polymerization temperature was controlled using a PID

temperature controller (Omega, CN-8502) with a heating jacket and a cooling U-coil (water as coolant) inside the reactor. The temperature was measured using a thermocouple (Omega, K-type) immersed in a thermowell, connected to the temperature controller unit. The rate of ethylene consumption was monitored by using a mass-flow meter (Cole-Parmer, Model No. 32915-14) linked to a computer (LABVIEW v5.5 software) to acquire the temperature and flow-rate data as a function of time.

Prior to each run, the reactor was dried at 150 ℃ under vacuum for 1 h. The temperature was cooled down while flushing with pure nitrogen for several times and ethylene for the last cycle. The stirring speed was constant at 1 000 rpm. All chemicals made as solutions in toluene were packed into a cylindrical bomb under an inert atmosphere to transfer into the reactor by N_2 over pressure. First, toluene and a desirable amount of MAO were added into the reactor. After stirring for 5 min, the operating temperature was set up to 50 ℃/80 ℃ and the prepared catalyst was directly charged into the reactor. Then the reactor was pressurized with ethylene at 0.1/0.4/0.8 MPa. After 0.5 h/1 h, the reactor was cooled to room temperature and depressurized. Ten milliliters of acidic methanol were injected into the reactor to quench the system. The final product was washed with an excess of methanol a few times, filtered, and left in the hood for 4 d.

1.4 Catalyst characterization

The bulk concentration of boron on the silica support was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES Leeman Labs Plasma-Spec ICP model 2.5). Samples for testing were prepared by digesting the catalyst powder in a 4 mol/L aqueous solution of HNO_3. A calibration curve was run prior to the samples, and an independent check was run interspersed with the samples.

1.5 Polymer characterizations

Gel Permeation Chromatography

The molecular weight and molecular weight distribution of polymers were determined using a high-temperature gel permeation chromatograph equipped with three Waters Ultrastyragel columns in series at 150 ℃ with *o*-dichlorobezene as the solvent. The columns were calibrated with narrow molecular weight distribution polystyrene samples.

Differential Scanning Calorimetry

The thermal behaviour of polymers was examined with a PerkineElmer Pyris Diamond DSC at standard heating/cooling rate of 10 ℃/min, under nitrogen flow. The samples were first melted to 170 ℃ (1st scan) and kept at this temperature for 3 min, then cooled to 25 ℃ and again heated up to the melting with the same heating rate (2nd scan). The reported melting temperature values are referred to the second heating scan. Temperatures and heats of phase transitions were determined, respectively, from the maxima and areas of the crystallization and melting peaks.

In this context, it was possible to relate $\triangle H_m$ (J/g) to the density (d, g/mL) of the polymer through the following semi-empirical equation: $d = (2\,195 + \triangle H_m)/2\,500$. The degree of crystallinity X_c of the polymer was calculated from the ratio between the values of melting enthalpy, $\triangle H_m$ (as calculated from the second heating scan) and the heat of fusion of 100% crystalline PE taken as $\triangle H_0 = 293$ J/g[17-18].

^{13}C NMR Spectroscopy

^{13}C NMR spectroscopy was used to determine the triad distribution and 1-hexene, 1-octene insertion indicating the copolymer microstructure. Sample solution was prepared by dissolving copolymer in deuterated o-dichlorobenzene. ^{13}C NMR spectra were taken at 333 K using Bruker Avance II 400 operating at 400 MHz with an acquisition time of 1.5 s and a delay time of 4 s. The test temperature was 135 ℃.

2 Results and discussion

The results of ethylene homopolymerization and ethylene/α-olefin copolymerization with the supported catalysts are listed in Table 1. From the results, it was found that when the added amount of boron was 5.1×10^{-4} mol/g SiO_2, the molar ratio of B : Zr was between14.10 ~ 19.04, the activity of the supported metallocene catalysts reached up to 10^7 g/(molZr · h) which was 511 ~ 1 090 times higher than that with MAO as the activator under the same conditions. The

Table 1 Catalytic activity of supported catalysts for ethylene homopolymerization and ethylene/α-olefin copolymerization

		Type of Activators					
		MAO[1]	MAO[2]	$B(C_6F_5)_3$	$[HNMe_2Ph]$-$[B(C_6F_5)_4]$	$[Ph_3C]$-$[B(C_6F_5)_4]$	$B(C_6F_5)_3$/TMA
Added amount	[Zr] /(10^{-4} mol/g SiO_2)	2.22	2.22	2.22	2.22	2.22	2.22
	[Al]or[B] (10^{-4} mol/g SiO_2)	82[a]	5.1[a]	5.1[b]	5.1[b]	5.1[b]	5.1[a]
Supported amount	[Zr]/(μmol)	13.15	5.48	8.77	24.12	25.21	12.06
	[Al] or [B][c]/(mmol)	0.20[a]	0.10[a]	0.16[b]	0.45[b]	0.48[b]	0.17[a]
	Al : Zr or B : Zr	15.21[a]	18.25[a]	18.24[b]	18.66[b]	19.04[b]	14.10[a]
Ethylene polymerization	Yield/ (g)	3.13	0.0010	1.01	3.52	4.02	1.12
	Activity/10^7 g/(molZr · h)	4.76	0.0036	2.30	2.92	3.19	1.86
Ethylene/1-hexene copolymerization	Yield /(g)	4.58	0.0014	1.97	6.50	7.13	2.41
	Activity/10^7 g/(molZr · h)	6.97	0.0051	4.49	5.39	5.68	4.00
Ethylene/1-octene copolymerization	Yield /(g)	3.57	0.0013	1.69	5.69	6.24	2.04
	Activity/10^7 g/(molZr · h)	5.43	0.0047	3.85	4.72	4.97	3.38

Polymerization conditions: toluene = 100 mL, MAO = 1.3 mL, m_{cat} = 10 mg, T_p = 50 ℃, ethylene = 0.1 MPa, time = 0.5 h, c(1-hexene) = 0.25 mol/L,
c(1-octene) = 0.25 mol/L.
a: For[Al]; b: For [B]; c: From ICP-AES analysis.

added amount of boron was only 1/16 of MAO for the same catalytic activity of 10^7 g/(mol Zr · h). It implied that the catalytic activity of the supported metallocene catalyst significantly increased when the boron compound was used as the activator. It is probably because boron compound have a stronger Lewis acidity, so the M-L bond was broken more easily and form a stable metallocene cationic center. Meanwhile the structure of fluorinated benzene ring can effectively reduce the electron density of the benzene ring, so the benzene ring is difficult to bind to the metallocene cationic center which greatly enhances the electrophilicity of the metallocene cationic active center. The coordination of the olefin monomer to the active center is more easily and thus the supported metallocene catalysts give higher activities in the olefin polymerization[19-21]. That the activity of ethylene/1-hexene and ethylene/1-octene copolymerization was higher than that of ethylene homopolymerization is due to the impact of "comonomer effect".

Figure 1 illustrates a proposed mechanism of funtionalization of boron compound ($B(C_6F_5)_3$, $[HNMe_2Ph][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$) on the silica support. However, it was found that the $B(C_6F_5)_3$/silica system showed lower activity. It is because that the binding of $B(C_6F_5)_3$ to the surface hydroxyl groups is reversible when washing with toluene during the preparation. It is due to the high solubility of $B(C_6F_5)_3$ in toluene and the fact that the anionic borane remains adducted to the support by electrostatic forces without anchoring via a covalent tether[15, 22-23]. The activity of the catalyst with $[HNMe_2Ph][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ as activator was higher than that of $B(C_6F_5)_3$. We suspect this may be because of weak coordination between $[HNMe_2Ph][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$ and metallocene cationic active center. It is attributed to that it is not the boron atom coordinated with the metallocene cationic active center but the fluorine atom on the fluorinated benzene ring. Also, the presence of the counter ion $[HNMe_2Ph]^+$ or $[CPh_3]^+$ resulted more stable metallocene cationic active center[19-21].

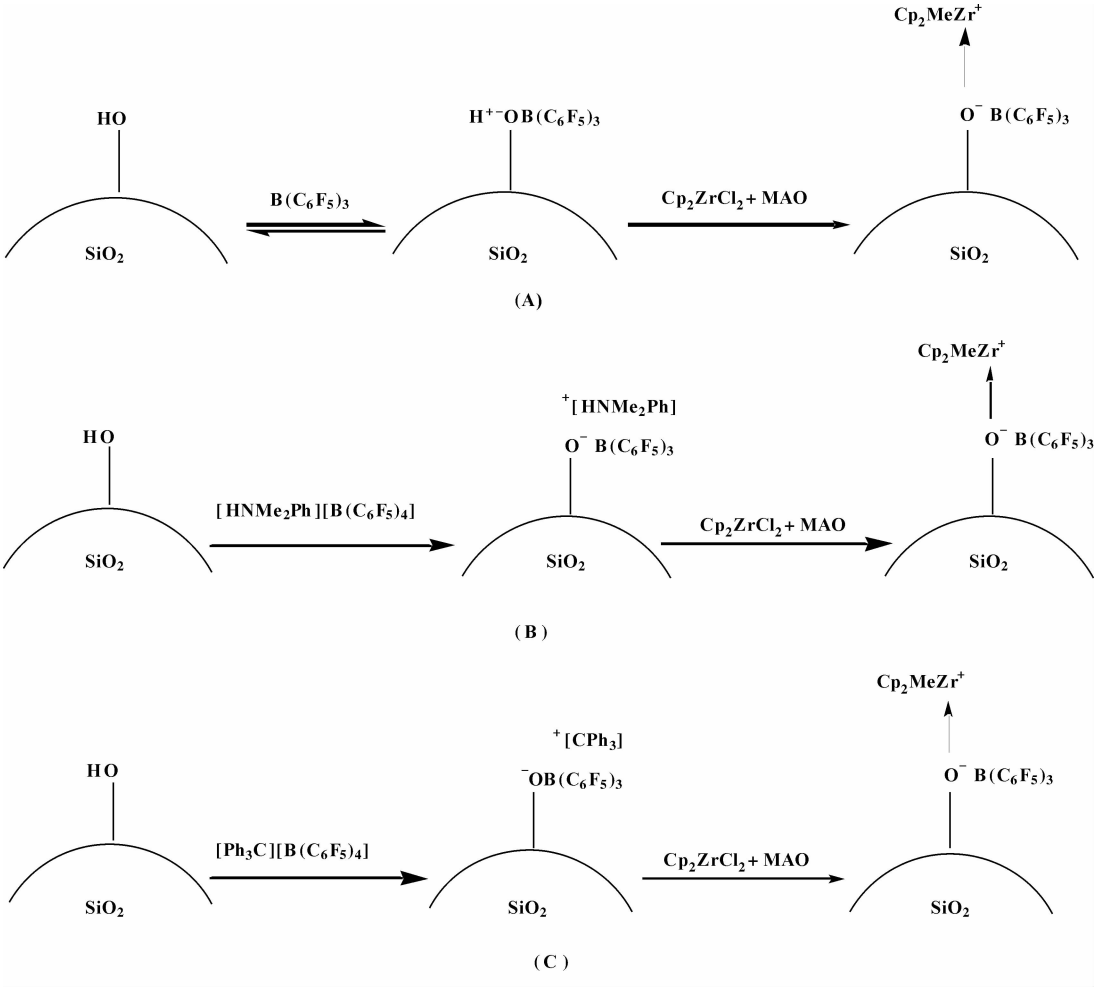

Fig. 1 Mechanisms of metallocene activation with supported borane activators:
(A) $H^+[B(C_6F_5)_3\text{-}SiO_2]^-$ (B) $[HNMe_2Ph]^+[B(C_6F_5)_3\text{-}SiO_2]^-$ and (C) $[CPh_3]^+[B(C_6F_5)_3\text{-}SiO_2]^-$

The activity of catalyst with the silica support treated by $B(C_6F_5)_3$/TMA was lower, probably because the proportion of the ion pair $Cp_2ZrCl—\mu\text{-}Cl—Al(C_6F_5)_2Me$ was larger when the $B(C_6F_5)_3$: TMA ratio was 1 : 1. Compared with $Al(C_6F_5)_3$, Lewis acidity of $Al(C_6F_5)_2Me$ was weaker. It was difficult for $Cp_2ZrCl—\mu\text{-}Cl—Al(C_6F_5)_2Me$ to dissociate resulting metallocene cation Cp_2ClZr^+, so the activity was lower[24].

The results of ethylene/1-hexene copolymerization catalyzed by the supported catalysts with $B(C_6F_5)_3$, $[HNMe_2Ph][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ as activators are listed in Table 2. As can be seen from Table 1 and Table 2, the polymerization activity of the supported catalyst increased with the increase of ethylene pressure and polymerization temperature. The activity of the supported metallocene catalysts was much higher than that with MAO as the activator under the same conditions. Compared with $B(C_6F_5)_3$, the activity of the supported catalyst with $[HNMe_2Ph][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ as activator was higher. Moreover, compared with $[HNMe_2Ph][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$, the ethylene/1-hexene copolymerization activity catalyzed by the supported catalyst using $B(C_6F_5)_3$ as activator increased with a lesser extent with the increase of ethylene pressure and polymerization temperature. This may be because of the increase of ethylene pressure and polymerization temperature, $B(C_6F_5)_3$ is more readily eluted from the carrier surface in the polymerization system leading to a reduction in polymerization activity.

Table 2 Catalytic activity of supported catalysts for ethylene/1-hexene copolymerization

Type of Activators	Yield[a] /(g)	Activity[a]/ 10^8 g/(molZr · h)	Yield[b] /(g)	Activity[b]/ 10^8 g/(molZr · h)
MAO[2]	–	–	0.1315	0.0240
$B(C_6F_5)_3$	16.58	1.89	29.91	3.41
$[HNMe_2Ph][B(C_6F_5)_4]$	62.47	2.59	126.15	5.23
$[Ph_3C][B(C_6F_5)_4]$	70.34	2.79	140.42	5.57

Polymerization conditions: toluene=500 mL, MAO=3.9 mL, m_{cat}=10 mg, T_p=80 ℃, a. ethylene=0.4 MPa; b. ethylene=0.8 MPa, time=1 h, c(1-hexene)=0.25 mol/L

The molecular weight and molecular weight distribution of the copolymers produced from ethylene/1-hexene and ethylene/1-octene copolymerization catalyzed by the supported catalysts mentioned above are listed in Table 3. It can be seen more intuitive from Figure 2(GPC curves of ethylene/1-hexene and ethylene/1-octene copolymer) that all of the copolymers produced from the supported catalysts have a narrow molecular weight distribution. The molecular weight distribution of the copolymers produced from the supported catalysts with $[HNMe_2Ph][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ as activators were narrower, and it was the narrowest with $[Ph_3C][B(C_6F_5)_4]$ as activator. It can be attributed to the more single metallocene cationic active species in the polymerization system. When $B(C_6F_5)_3$ was used as the activator, metallocene cationic active centers easily changed resulting more metallocene cationic species in the polymerization system. Therefore, the molecular weight distribution is relatively broader.

Table 3 The M_w and M_w/M_n of polymer

Type of Activators	Ethylene/1-hexene		Ethylene/1-octene	
	$M_w(\times10^4)$	M_w/M_n	$M_w(\times10^4)$	M_w/M_n
MAO	7.25	2.40	11.44	2.46
$B(C_6F_5)_3$	11.11	3.07	10.85	3.29
$[HNMe_2Ph][B(C_6F_5)_4]$	10.48	2.33	6.75	2.34
$[Ph_3C][B(C_6F_5)_4]$	11.06	2.12	9.10	2.16
$B(C_6F_5)_3$/ TMA	9.77	2.83	11.93	2.80

Polymerization conditions: toluene=100 mL, MAO=1.3 mL, m_{cat}=10 mg, T_p=50 ℃, ethylene=0.1 MPa, time=0.5 h, c(1-hexene)=0.25 mol/L, c(1-octene)=0.25 mol/L.

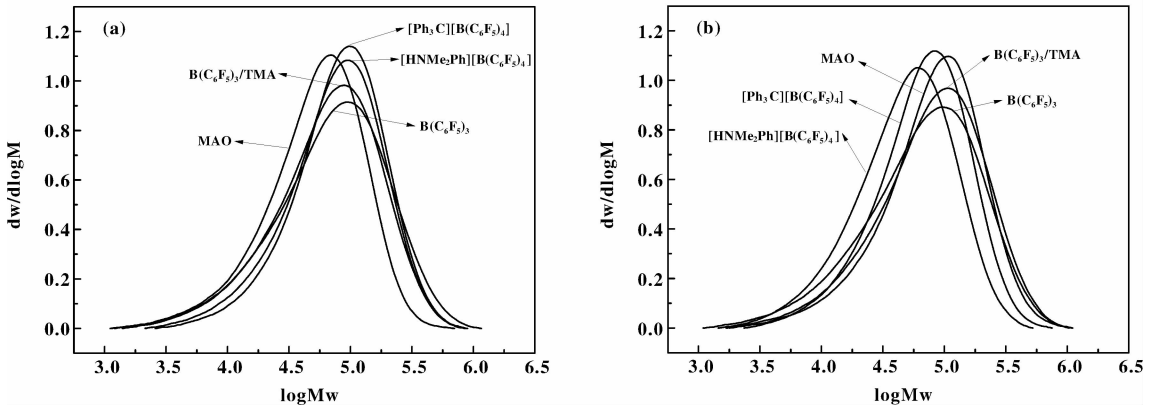

Fig. 2 GPC curves of ethylene/1-hexene copolymer (a) and ethylene/1-octene copolymer (b)

Thermal performance parameters of the polymer products are shown in Table 4. The order of the melting point of the ethylene/1-hexene copolymers was $B(C_6F_5)_3$/TMA > $[Ph_3C][B(C_6F_5)_4]$ > MAO > $[HNMe_2Ph][B(C_6F_5)_4]$ > $B(C_6F_5)_3$ and the order of the crystallinity was $[Ph_3C][B(C_6F_5)_4]$ > $B(C_6F_5)_3$/TMA > MAO > $[HNMe_2Ph][B(C_6F_5)_4]$ > $B(C_6F_5)_3$. And compared with ethylene homopolymerization, melting point and crystallinity of the copolymer decreased significantly with the addition of 1-hexene or 1-octene comonomer. Compared with ethylene/1-hexene copolymers, the melting point and crystallinity of the ethylene/1-octene copolymers were lower due to the longer branch chain in the polymer chains. The density of the copolymers was between 0.91 ~ 0.92 g/cm^3 which belonged to the scope of mLLDPE[17-18].

Table 4 Thermal performance parameters of polymer

Type of Activators	Monomer	T_m/(℃)	ΔH_m/(J·g^{-1})	X_c/(%)	d/(g·cm^{-3})
MAO	Ethylene	127.05	152.70	52.12	0.94
MAO	Ethylene/1-hexene	105.58	88.06	30.05	0.91
MAO	Ethylene/1-octene	105.44	87.57	29.89	0.91
$B(C_6F_5)_3$	Ethylene/1-hexene	104.48	80.70	27.54	0.91
$[HNMe_2Ph][B(C_6F_5)_4]$	Ethylene/1-hexene	105.50	86.77	29.61	0.91
$[Ph_3C][B(C_6F_5)_4]$	Ethylene	127.44	161.91	55.26	0.94
$[Ph_3C][B(C_6F_5)_4]$	Ethylene/1-hexene	106.61	98.10	33.48	0.92
$[Ph_3C][B(C_6F_5)_4]$	Ethylene/1-octene	102.85	81.79	27.92	0.91
$B(C_6F_5)_3$/ TMA	Ethylene/1-hexene	107.64	95.68	32.66	0.92

Polymerization conditions: toluene = 100 mL, MAO = 1.3 mL, m_{cat} = 10 mg, T_p = 50 ℃, ethylene = 0.1 MPa, time = 0.5 h, c(1-hexene) = 0.25 mol/L, c(1-octene) = 0.25 mol/L.

Fig. 3 shows the ^{13}C-NMR spectrum of ethylene/1-hexene copolymer obtained with $[Ph_3C][B(C_6F_5)_4]$. The sequence distribution of ethylene/1-hexene copolymer which was calculated according to literature[25-26] was shown in Table 5. Monomer content (%E, %H), average sequence length (n_E, n_H) and reactivity ratios (rE·rH) of ethylene/1-hexene copolymers were shown in Table 6.

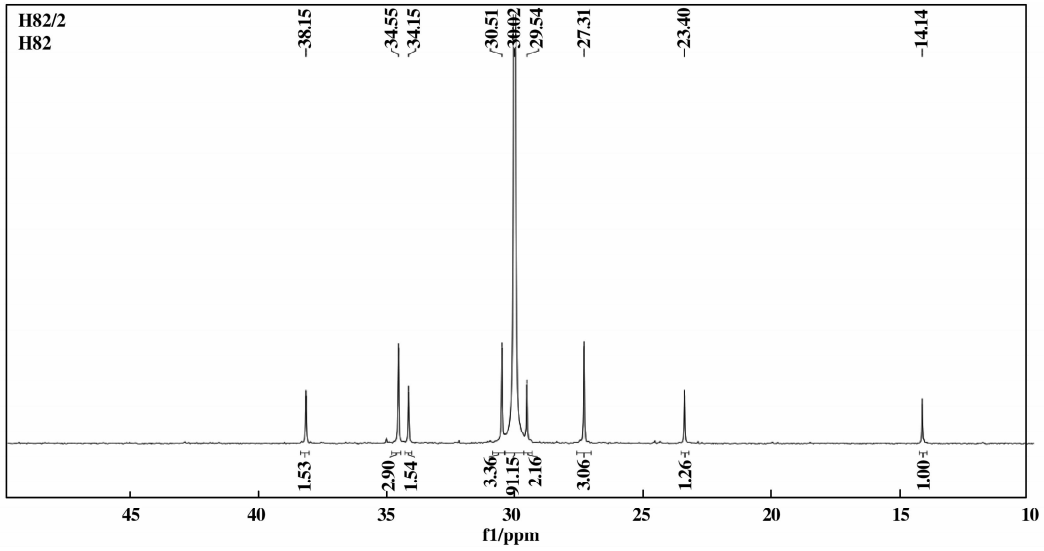

Fig. 3 ^{13}C-NMR spectrum of ethylene/1-hexene copolymer obtained with $[Ph_3C][B(C_6F_5)_4]$

Table 5 Sequence distribution of ethylene/1-hexene copolymer

Type of Activators	Diad distributions			Triad distributions					
	HH	EH	EE	HHH	HHE	HEH	EHE	EEH	EEE
MAO	0	0.0576	0.9389	0	0	0	0.0288	0.0646	0.9066
$B(C_6F_5)_3$	0	0.0574	0.9428	0	0	0	0.0287	0.0570	0.9143
$[HNMe_2Ph][B(C_6F_5)_4]$	0	0.0520	0.9453	0	0	0	0.0260	0.0575	0.9165
$[Ph_3C][B(C_6F_5)_4]$	0	0.0594	0.9406	0	0	0	0.0297	0.0594	0.9109
$B(C_6F_5)_3$/TMA	0	0.0592	0.9451	0	0	0	0.0296	0.0507	0.9197

Polymerization conditions: toluene = 100 mL, MAO = 1.3 mL, m_{cat} = 10 mg, T_p = 50 ℃, ethylene = 0.1 MPa, time = 0.5 h, c(1-hexene) = 0.25 mol/L

Table 6 Monomer content & average sequence length & reactivity ratios of ethylene/1-hexene copolymer

Type of Activators	%E	%H	n_E	n_H	rE · rH
MAO	97.12	2.88	30.07	1	0
$B(C_6F_5)_3$	97.13	2.87	34.08	1	0
$[HNMe_2Ph][B(C_6F_5)_4]$	97.40	2.60	33.88	1	0
$[Ph_3C][B(C_6F_5)_4]$	97.03	2.97	32.67	1	0
$B(C_6F_5)_3$/ TMA	97.04	2.96	38.28	1	0

Polymerization conditions: toluene = 100 mL, MAO = 1.3 mL, m_{cat} = 10 mg, T_p = 50 ℃, ethylene = 0.1 MPa, time = 0.5 h, c(1-hexene) = 0.25 mol/L

As can be seen from Table 6, comonomer content of ethylene/1-hexene copolymers produced from the supported catalysts was between 2.60% ~ 2.97%. The comonomer content was the highest with $[Ph_3C][B(C_6F_5)_4]$ activator. The average sequence length of ethylene unit was the highest for $B(C_6F_5)_3$/TMA activator (38.28) and the lowest for MAO activator (30.07). The average sequence length of 1-hexene unit is approximately 1. Triad [HHH] and [HHE] content was almost zero, indicating the absence of a long 1-hexene sequence structure in the copolymer, and that 1-hexene comonomer inserted into the polymer chains randomly. The structure of the copolymers can be determine by the rE · rH value, if rE · rH>1, it tends to be block copolymers, if rE · rH<1, it tends to be random copolymers, if rE · rH = 0, it tends to be alternating copolymers[25, 27-28]. The rE · rH value was almost 0 (0<rE · rH<1) owing to the rH value was almost 0.

3 Conclusions

When the added amount of boron was 5.1 × 10^{-4} mol/g SiO_2, the B : Zr ratio was between 14.10 ~ 19.04, the activity of the supported metallocene catalysts reached up to 10^7 g/(mol Zr · h) which was 511 ~ 1 090 times higher than that with MAO as the activator under the same conditions. The added amount of boron was only 1/16 of MAO for the same catalytic activity of 10^7 g/(mol Zr · h). Compared with the supported catalyst with $B(C_6F_5)_3$ as activator, the catalytic activity of supported metallocene catalyst with $[HNMe_2Ph][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ as activator was higher. It was also found that $[Ph_3C][B(C_6F_5)_4]$ system had the most narrow molecular weight distribution (MWD) and maximum 1-hexene content (2.97%). Copolymers prepared by the supported metallocene catalysts with boron activators had narrow MWD and density between 0.91 ~ 0.92 g/cm^3

which belonged to the scope of mLLDPE.

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以硼化物为活化剂制备负载茂金属催化剂催化乙烯均聚和乙烯/α-烯烃共聚合

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摘要: 以硅胶为载体,以 Cp_2ZrCl_2 为主催化剂,分别以甲基铝氧烷(MAO)、三五氟苯基硼($B(C_6F_5)_3$)、N,N-二甲基苯铵四(五氟苯基)硼酸盐([$HNMe_2Ph$][$B(C_6F_5)_4$])、三苯碳鎓四(五氟苯基)硼酸盐([Ph_3C][$B(C_6F_5)_4$])、三五氟苯基硼/三甲基铝($B(C_6F_5)_3$/TMA)为活化剂制备了负载茂金属催化剂,考察了它们对乙烯均聚、乙烯/α-烯烃共聚合的影响. 实验结果表明,当硼化物用量为 5.1×10^{-4}mol/g SiO_2, B/Zr 在 14.10 ~ 19.04 之间时,负载茂金属催化剂催化烯烃聚合活性达 10^7g/(molZr · h),是相同条件下以 MAO 为活化剂时活性的 511 ~ 1 090 倍,同样达到 10^7g/(molZr · h)的催化活性,硼化物用量仅仅为 MAO 用量 1/16;和 $B(C_6F_5)_3$ 相比,以[$HNMe_2Ph$][$B(C_6F_5)_4$]和[Ph_3C][$B(C_6F_5)_4$]为活化剂制备的负载茂金属催化剂活性较高,并且以[Ph_3C][$B(C_6F_5)_4$]为活化剂制备的负载茂金属催化剂所得共聚物分子量分布最窄,乙烯/1-己烯共聚物中共单体含量最高,为2.97%;采用硼化物为活化剂制备的负载茂金属催化剂催化乙烯/1-己烯、乙烯/1-辛烯共聚合所得共聚产物分子量分布较窄,密度在 0.91 ~ 0.92 g/cm^3 之间,属于 mLLDPE 范畴.

关键词: 负载茂金属催化剂;硼;乙烯;α-烯烃;共聚