Preparation of spherical MgCl$_2$-supported bis(phenoxy-imine) zirconium complex for ethylene polymerization

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Abstract

The spherical MgCl$_2$ supports treated by methylaluminoxane (named MAO-supports) were prepared using MgCl$_2$·2.56C$_2$H$_5$OH adducts as support material subjected to elimination of EtOH by thermal dealcoholization treatments. Then bis(phenoxy-imine) zirconium complex, bis-[*N*-(3-*tert*-butylsalicylidene)cyclohexylaminato] zirconium(IV) dichloride (**1**), was directly impregnated onto these MAO-supports. ICP, EDX, GC, N$_2$-BET, IR and XRD analyses indicated that the texture of the supports and MAO-supports, the elements on solid catalysts, and so on, were greatly relied on dealcoholization temperature. Meanwhile, it was also found that the activities of the supported catalysts for ethylene polymerization and the properties of resultant polymers were strongly dependent on dealcoholization temperature. Finally, PEs with spherical morphology and high bulk density (over 0.35 g/ml) were obtained, without reactor fouling.
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Keywords: Phenoxy-imine ligand; Zr complex; MgCl$_2$; Ethylene polymerization; Support

1. Introduction

Over the past decade, non-metallocene catalyst systems for olefins polymerization were developing rapidly owing to the diversification and performance of their ligands [1,2]. Grubbs synthesized a nickel complex with phenoxy-imine ligand for ethylene polymerization [3]. Furthermore, Fujita and his coworkers have successfully established highly active Ti/Zr catalysts using various substituted phenoxy-imine ligands for olefin polymerization, which were named FI catalysts, and the activity of these FI catalysts is one of the highest for ethylene polymerization among not only non-metallocene but also other olefin polymerization catalysts [4]. FI catalysts with MAO or with *i*-Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ co-catalysts are capable of producing many distinctive polymers with high efficiency, such as vinyl-terminated low molecular weight PEs and exceptionally high molecular weight PEs [4e], well-defined multi-modal molecular weight distribution polyethylene [5], and so on.

Recently we [6] found some alkylaluminums, such as triethylaluminum (Et$_3$Al), trihexylaluminum (He$_3$Al), or trimethylaluminum (Me$_3$Al), could activate bis(phenoxy-imine) Zr and Ti complexes for ethylene polymerization without MAO or Ph$_3$CB(C$_6$F$_5$)$_4$. The activity of bis(phenoxy-imine) Zr complex/trialkylaluminum approaches that of bis(phenoxy-imine) Zr complex/MAO.

Up to now, pioneering researchers have been making great strides in the field of supporting single-site catalysts on spherical MgCl$_2$ support [7,8]. To the best of our knowledge, there has been no report on spherical MgCl$_2$-supported bis(phenoxy-imine) zirconium catalyst system for ethylene polymerization. An alternative approach, developed by Fujita and co-workers [9], was the reaction of Al*i*Bu$_3$ with a hydrocarbon solution of MgCl$_2$/2-ethylhexanol adduct, leading to the precipitation of a MgCl$_2$/Al*i*Bu$_n$ (OR)$_{3-n}$ support. These supports had been shown to be effective for the activation of Ti-, Zr- and V-based FI catalysts, giving well-defined polymer particle morphology and activities comparable to those obtained via activation with MAO.

In this paper, we have explored an effective method for immobilizing bis(phenoxy-imine) zirconium complex, bis-[*N*-(3-*tert*-butylsalicylidene)cyclohexylaminato] zirconium(IV) dichlo-

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ride (**1**), on spherical MgCl$_2$ supports. The resultant solid catalyst was proved to be very active in ethylene polymerization, leading to the formation of spherical polymer particles with high bulk density.

2. Experimental part

2.1. Materials

All manipulation involving air- or moisture-sensitive compounds was carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a conventional nitrogen-filled glovebox. Toluene was refluxed over sodium/benzophenone ketyl and distilled under nitrogen before use. Hexane was dried over 4-Å molecular sieves. Ethylene was obtained from the Yanshan Petrochemical Corporation, China Petroleum & Chemical Corporation. Et$_3$Al (TEA) was purchased from Crompton Corp., and diluted into 2.0 M solution in hexane. MAO was purchased from Crompton Corp., as a 10 wt.% solution in toluene, and used as received.

Bis-[*N*-(3-*tert*-butylsalicylidene) cyclohexylaminato] zirconium(IV) dichloride (**1**) was synthesized by the reaction of ZrCl$_4$(THF)$_2$ with two equivalents of the lithium salt of the corresponding phenoxy-imine ligands according to the literature [4d].

2.2. Preparation of spherical MgCl$_2$ adducts

According to Ref. [10], the practical preparation was done as follows: first, in a three-necked, 250-ml flask with a mechanical stirrer, 21.3 g MgCl$_2$ was completely dissolved in 37.8 ml ethanol at 70–80 °C and then dispersed in the medium of a mixture of 75 ml white oil and 75 ml methyl silicon oil at 120 °C. Then the mixture was transferred into another flask, which contained a mixture of 112.5 ml white oil and 112.5 ml silicon oil at 120 °C. There, the MgCl$_2$ solution was stirred strongly for 3 min with an rpm of 3500 at 120 °C. In the end, the resultant mixture was introduced into 1600 ml of *n*-hexane at −25 °C, and the MgCl$_2$ alcohol support was recrystallized, rinsed with *n*-hexane three times. After dried *in vacuo*, 43.5 g product was collected in a nitrogen atmosphere. By test, its composition was MgCl$_2$·2.56C$_2$H$_5$OH and its mean particle size was 59.6 μm.

2.3. Support thermal dealcoholization treatments

The MgCl$_2$·2.56C$_2$H$_5$OH supports were thermally pretreated at 110, 130, 140, 150, 160 and 170 °C under nitrogen for 4 h in a fluidized bed reactor, respectively. The corresponding resultant pre-supports were named SP-1, SP-2, SP-3, SP-4, SP-5 and SP-6. The original spherical MgCl$_2$·2.56C$_2$H$_5$OH support was named SP-0.

2.4. MAO-support preparation

The MAO-supports were prepared according to the following typical procedure: 23 ml MAO was added to 5.0 g corresponding pre-support in 35 ml of toluene, followed by vigorous stirring of

mixture at room temperature for 1 h, then the mixture was heated to 50 °C. After reacting for 4 h at 50 °C, the resulted solid part, collected by filtration, was washed three times with 20 ml of toluene and three times with 50 ml of hexane, and then dried under N$_2$ until taking on free flowing state. The resultant MAO-supports were named MSP-1, MSP-2, MSP-3, MSP-4, MSP-5 and MSP-6, which were prepared from SP-1, SP-2, SP-3, SP-4, SP-5, SP-6, respectively.

2.5. Catalyst preparation

Supported catalysts were prepared according to the following typical procedure: 1.0 g corresponding MAO-support was placed in the flask containing 5.0 ml toluene and the slurry was stirred at constant temperature of 30 °C, then a certain toluene solution of complex 1 (5 μmol/100 mg MAO-support) was added to the slurry slowly. After stirring for 1 h at 30 °C, the liquid phase was removed, and the solid residue was washed twice with 5.0 ml of toluene and washed with hexane until the liquid phase was colorless. The solid catalyst was dried under N$_2$ until taking on free flowing state. The resultant solid catalysts were named MPSC-1, MPSC-2, MPSC-3, MPSC-4, MPSC-5 and MPSC-6, which were prepared from MSP-1, MSP-2, MSP-3, MSP-4, MSP-5, MSP-6, respectively.

2.6. Polymerization runs

The polymerization of ethylene was performed in a stainless steel autoclave (2.0 l capacity) equipped with gas ballast through a solenoid valve for continuous feeding of ethylene at constant pressure while using hexane as solvent. Purified hexane (1.0 l) was transferred to the reactor under nitrogen atmosphere. The TEA was employed as compensatory cocatalyst as well as scavenger in the polymerization system. Then the suspension of solid catalyst was injected into the reactor using a syringe. As the set temperature was reached, the reactor with ethylene was pressurized to initiate the polymerization for set reaction time. At the end of the reaction, ethylene pressure was released and the granular polyethylene was separated from the reactor mixture by filtration and dried in an oven at 40 °C for 8 h.

2.7. Characterization of ethylene polymerization process

Ethylene consumption was measured by a mass flowmeter, and the data were recorded every 5 min. The final activities of supported catalysts were calculated by measuring the mass of the resultant polymers.

2.8. Characterization of the supports, MAO-supports, the supported catalysts and polymers

The IR spectra were recorded on the Magna-IR spectrophotometers. The samples for IR examination were prepared in glove box as Nujol mulls in KBr pellets.

The morphologies of the supports, the supported catalysts and PE particles were investigated using a Philips environmental scanning electron microscope XL-30 ESEM FEG (Philips, The

Table 1
Characteristics of pre-supports and MAO-supports

Entry	Pre-supports			MAO-supports			
		Dealcoholization temperature (°C)	Residual ethanol (wt.%)		BET surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter (nm)
1	SP-1	110	37.3	MSP-1	–	–	–
2	SP-2	130	13.0	MSP-2	7.130	0.010	0.620
3	SP-3	140	10.5	MSP-3	–	–	–
4	SP-4	150	8.2	MSP-4	138.467	0.015	0.605
5	SP-5	160	3.2	MSP-5	100.232	0.017	2.163
6	SP-6	170	2.2	MSP-6	4.171	0.015	2.175
7	–	–	–	SP-6	95.320	0.560	15.385

Netherlands, now Fei Co.) equipped with an energy-dispersive X-ray spectrometer (EDX) for the distribution of Al and Zr on the carrier. The samples for EDX analysis were prepared according to the literature [7a], and then they were initially fixed on a carbon tape ad then coated with carbon by conventional sputtering techniques. Elemental content was performed with ICP-AES.

The specific surface areas and porosity were measured by the N_2-BET method with CE SORPTOMATIC 1990. The ethanol content of the support was determined by means of GC. Powder X-ray diffraction (XRD) patterns of the original support, pre-supports and MAO-supports were obtained with Rigaku D/max 2500 VB2+/PC instrument equipped with a source using Cu anode, operating at 40 kV and 40 mA for Cu $K\alpha_1$ radiation. The dried sample was covered with a thin PE film to avoid contacting with air and moisture. The diffraction pattern was recorded in the range, $5° < 2\theta < 70°$, with a scanning speed of 3°/min.

Molecular weight and molecular weight distribution (M_w/M_n, MWD) of the PE were measured by means of gel permeation chromatography (GPC) on a Waters Alliance GPCV2000 at 150 °C with 1,2,4-$C_6H_3Cl_3$ as eluant.

3. Results and discussion

3.1. Effect of dealcoholization temperature on the supports

As shown in Table 1, the content of ethanol in $MgCl_2 \cdot 2.56C_2H_5OH$ decreases with increasing the dealcoholization temperature. When treated at 170 °C for 4 h, the support (SP-6), with a surface area of 95.320 m^2/g and pore volume 0.560 ml/g, was obtained. Moreover, as indicated in Table 1, dealcoholization temperature markedly influences the surface area and porosity of the resultant MAO-supports. When the support was pretreated at lower or higher temperature, the corresponding MAO-support shows very low surface area.

The original support ($MgCl_2 \cdot 2.56C_2H_5OH$), pre-supports and MAO-supports were tested by XRD, and the patterns are shown in Fig. 1. From Fig. 1, it reveals that the crystal structure of various supports is different with different dealcoholization temperature. The diffraction pattern of original support is more complicated than those of the thermally treated supports (pre-supports), indicating that $MgCl_2 \cdot 2.56C_2H_5OH$ adducts support

is a kind of polycrystalline solid. In the case of the support subjected to thermal pretreatment, the XRD pattern reflects substantial dealcoholation of the original support. Compared with the XRD pattern of SP-2, SP-3 and SP-4, the diffraction peaks of SP-5 and SP-6 disappeared at $2\theta < 15°$, which revealed that the feature of $MgCl_2/C_2H_5OH$ adducts has disappeared at these situations.

As shown in Fig. 1, when those supports obtained by thermal dealcoholation of $MgCl_2 \cdot 2.56C_2H_5OH$ at lower dealcoholation temperature (<170 °C) were modified by MAO at 50 °C for 4 h, the diffraction patterns of the resultant MAO-supports are all with a broad peak in the range of $30° < 2\theta < 35°$, suggesting that the crystal aggregates of these pre-supports had been destroyed after MAO modification, suggesting that MAO has reacted with the residual ethanol in supports. So, it can be concluded that the reaction between MAO and the residual ethanol in supports is a very important manner to get MAO fixed on the carrier.

It is worth noting that the XRD patterns of MSP-6 are similar to that of SP-6, which indicates that no violent reaction took place between SP-6 and MAO, owing to the lower content of residual ethanol in SP-6. As a result, the crystal aggregates of SP-6 were retained. As shown in Table 1, the surface
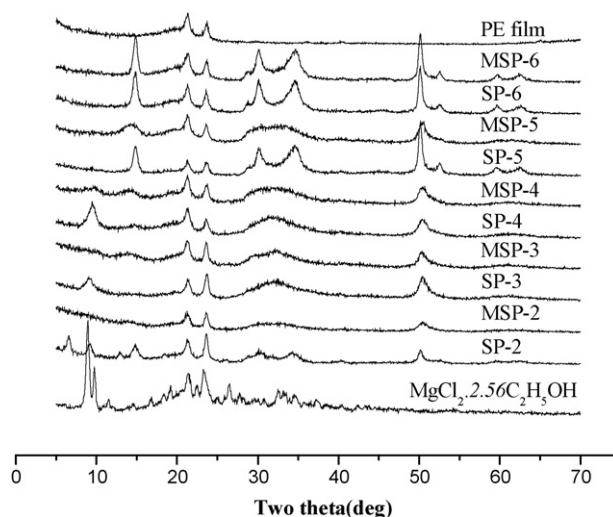

Fig. 1. XRD patterns of $MgCl_2 \cdot 2.56C_2H_5OH$, pre-supports and MAO-supports (corresponding to Table 1).
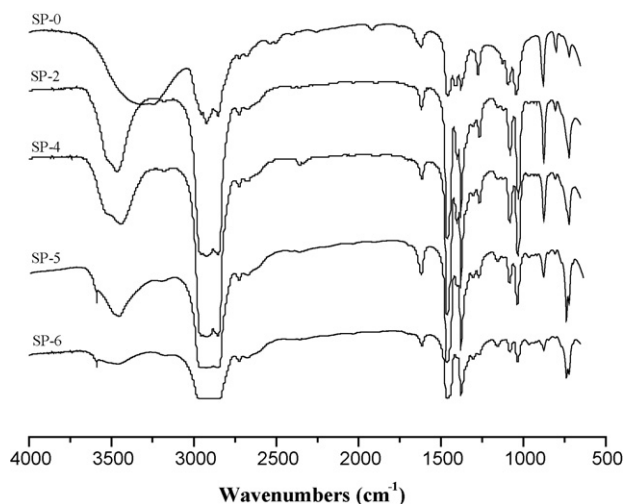
Fig. 2. IR spectra of original support and pre-supports (corresponding to Table 1).

Fig. 3. IR spectra of MAO-supports (corresponding to Table 1).

area and porosity of MSP-6 all decrease after MAO modification, suggesting that the original pores were almost filled with MAO.

The IR spectra gave also some related results in correspondence to the group of supports and MAO-supports investigated by XRD. Fig. 2 presents IR spectra recorded for original support and pre-supports. The absorption band around $3320 \, cm^{-1}$, which can be related to the O-H stretching, is very broad for $MgCl_2 \cdot 2.56C_2H_5OH$ (SP-0) and it becomes more narrow after a thermal dealcoholation. This suggests, as Fig. 2 confirms, a large extent of hydrogen bond character for SP-0 [11]. But for SP-2, SP-4, SP-5 and SP-6, the number of such bonds decreases, as a result, νO–H band was shifted to higher frequency around $3440 \, cm^{-1}$. The band at $1411 \, cm^{-1}$ is assigned to the feature peak of $MgCl_2 \cdot 2.56C_2H_5OH$ (SP-0) [12]. As indicated in Fig. 2, when PS-0 was pretreated at lower dealcoholation temperature ($\leq 150\,^\circ C$ in this work), the feature peak at $1411 \, cm^{-1}$ still exists, suggesting the support still is attributed to $MgCl_2$/ethonal adducts support at these situations, which is good in agreement with the results investigated by XRD. However, the feature peak disappeared when SP-0 was pretreated at higher dealcoholation temperature ($\geq 160\,^\circ C$ in this work), suggesting the support is attributed to $MgCl_2$ support at these situations, which is also consistent with the results obtained by XRD. While there still is a weak peak at about $3458 \, cm^{-1}$ for SP-6, suggesting that EtOH was not completely removed even at $170\,^\circ C$. At the same time, it demonstrates that the residual ethanol has been strongly coordinated to $MgCl_2$ after a high dealcoholation temperature.

Fig. 3 shows the IR spectra of MSP-2, MSP-4, MSP-5 and MSP-6. In this work, $MgCl_2 \cdot 2.56C_2H_5OH$ was thermally pretreated at different dealcoholization temperature, followed by the reaction with MAO. As obviously shown in Fig. 3, the O–H peak intensity of the supports is reduced dramatically and the feature peak at $1411 \, cm^{-1}$ has disappeared after modified by MAO. Meanwhile, as shown in Fig. 3, the Al–O group on MSP-2, MSP-4, MSP-5 or MSP-6 is clearly visible by the presence of
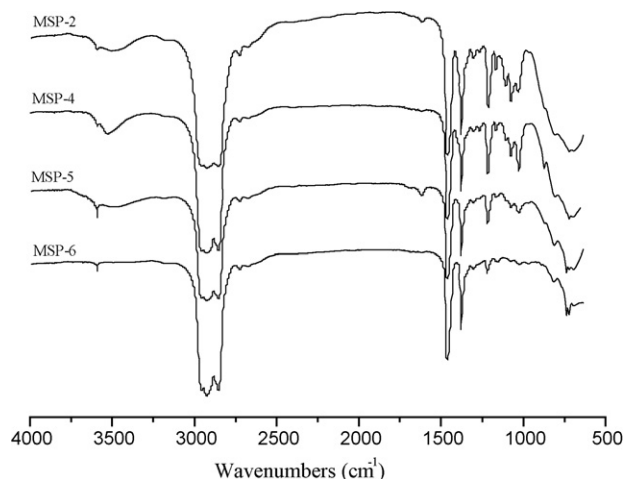
the 808 and $720 \, cm^{-1}$ [12]. These indicate that MAO was fixed on the carrier through the reaction with the residual ethanol in supports, which is in agreement with the results obtained by XRD.

3.2. Effect of dealcoholization temperature on the elements of the catalysts

Dealcoholization temperature not only determined the element content on the solid catalyst, but also influences the element distribution on the carrier.

As indicated in Table 2, the Al content on the solid catalysts decreased with the reducing residual ethanol in the support, suggesting that MAO was fixed on the carrier by the reaction with the residual ethanol of the support, which is consistent with the results investigated by XRD and IR. Compared with MSPC-4, -5 and -6, MSPC-2 has the highest Al loading, but the corresponding Zr content was the lowest. This may be due to the fact that MSP-2, as shown in Table 1, has very low surface area and porosity, which is difficult to make complexes impregnated into the carrier. To testify this hypothesis, X-ray spectrometer (EDX) was carried out for MSPC-2. As presented in Table 3, the amount of Zr is 0.54 wt.% on the surface of MSPC-2, but the inside is too low to be detected.

It also can be seen from Table 2, when $MgCl_2 \cdot 2.56C_2H_5OH$ (SP-0) was pretreated at higher dealcoholization tempera-

Table 2
Characteristics of catalysts

Entry	Pre-supports		Catalysts		
		Residual ethanol (wt.%)		Al (wt.%)	Zr (wt.%)
1	SP-1	37.3	MSPC-1	–	–
2	SP-2	13.0	MSPC-2	14.18	0.05
3	SP-3	10.5	MSPC-3	–	–
4	SP-4	8.2	MSPC-4	8.41	0.32
5	SP-5	3.2	MSPC-5	5.05	0.30
6	SP-6	2.2	MSPC-6	3.51	0.28

Table 3
The elements distribution on/in the catalysts determined by EDX[a]

Entry	Elements	Relative element content (wt.%)					
		MSPC-2		MSPC-4		MSPC-5	
		Surface	Inside	Surface	Inside	Surface	Inside
1	Mg	16.22	19.72	18.68	20.38	19.94	22.41
2	Cl	56.24	60.26	67.57	66.72	67.77	72.21
3	Al	27.00	20.02	13.18	12.90	11.83	4.89
4	Zr	0.54	0.00	0.57	0.00	0.46	0.49

[a] The contents of O and C were excluded.

ture, the Zr and Al contents on the solid catalysts decrease with increasing dealcoholization temperature. Combined with Tables 2 and 3, the Al and Zr contents of MSPC-4 are all higher than that of MSPC-5, but the element distribution shows big difference between them. As shown in Table 3, though the amount of Zr is as high as 0.57 wt.% on the surface of MSPC-4, the inside is too low to be detected, suggesting that active species mainly accumulated at the surface layer. On the contrary, the surface Zr loading of MSPC-5 is nearly equal to that of the inside, suggesting that active species have been evenly distributed on the whole catalyst. This may be due to the different textural properties between MSP-4 and MSP-5. As indicated in Table 1, MSP-4 has higher surface area, but its average pore diameter is as small as 0.605 nm, which is difficult to get complexes impregnated into the inside of the support. However, MSP-5 not only has high surface area but also has big pore diameter, which is helpful to distribute the active species on the whole carrier evenly.

3.3. Effect of dealcoholization temperature on the catalytic activity and polymer properties

Table 4 summarizes the ethylene polymerization activities of the supported catalysts and the properties of the resultant PEs. As indicated in Table 4, the activities of supported catalysts and the bulk density of the resultant PEs are strongly dependent on dealcoholization temperature, while dealcoholization temperature also influences the molecular weight and molecular weight distribution of the resultant polymers. When the support was thermally pretreated at lower temperature, the resultant

solid catalysts, such as MSPC-1, MSPC-2 and MSPC-3, were inactive for ethylene polymerization. On the contrary, when the support was pretreated at higher temperature, the corresponding solid catalysts, such as MSPC-4, MSPC-5 and MSPC-6, were all active for ethylene polymerization. It is noteworthy that, though the Al and Zr contents of MSPC-4 are all higher than that of MSPC-5 (as shown in Table 2), MSPC-4 exhibits lower activity than that of MSPC-5. This may be ascribed to the fact that the active species mainly accumulated at the surface layer of MSPC-4 (as shown in Section 3.2), which is apt to cause bimolecular catalyst deactivation processes like supported metallocene catalysts [13], resulting in a lower activity catalyst.

As shown in Fig. 4a, though MSPC-4 is a spherical granule, the resultant PE particles are fragmented (Fig. 4c and d), owing to the uneven distribution of active species on the catalyst (as shown in Section 3.2). A particularly important feature of any immobilized catalyst for olefin polymerization is the ability to give controlled particle size and morphology. As indicated in Fig. 4b, MSPC-5 is a spherical granule, and ethylene polymerization with it resulted in spherical polymer particle morphology (Fig. 4e and f), similar to that of MSPC-5, without reactor fouling. This is due to the fact that, as mentioned in Section 3.2, the active species are evenly distributed on the whole MSPC-5 against bimolecular catalyst deactivation processes. So the polymerization can take place outside and inside of the catalyst almost simultaneously. In this way, the solid catalysts, MSPC-5, can produce PEs with high productivity, good morphology and high bulk density [14]. Meanwhile, This confirms that the spherical morphology of the original support can be retained

Table 4
Ethylene polymerization catalyzed by supported 1 catalysts[a]

Entry	Pre-supports	Dealcoholization temperature (°C)	Catalysts	Activity (gPE/g cat)	Activity (gPE/mol Zr h)	Bulk density (g/ml)	M_w ($\times 10^4$)	MWD
1	SP-1	110	MSPC-1	Trace	–	–	–	–
2	SP-2	130	MSPC-2	Trace	–	–	–	–
3	SP-3	140	MSPC-3	Trace	–	–	–	–
4	SP-4	150	MSPC-4	692	1.96×10^7	0.35	8.5	8.24
5	SP-5	160	MSPC-5	968	2.93×10^7	0.36	2.5	3.29
6	SP-6	170	MSPC-6	540	1.75×10^7	0.39	2.1	3.80

[a] Polymerization conditions: 100 mg of catalyst, 3.0 mmol TEA as the scavenger and alkylating reagent, ethylene pressure = 1.0 MPa, polymerization temperature = 80 °C, solvent = 1000 ml hexane, polymerization time = 0.5 h.
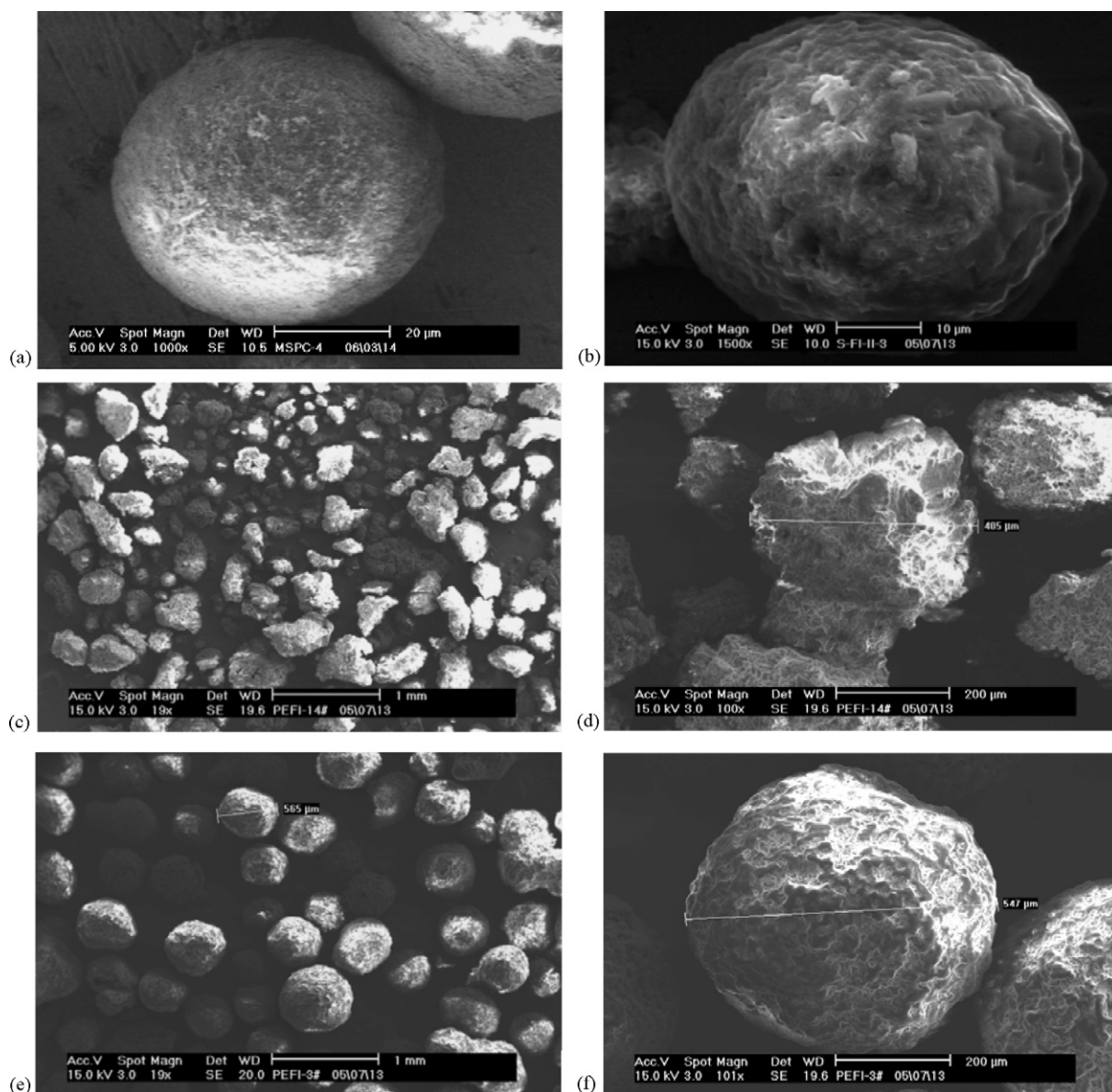
Fig. 4. SEM images of: (a) MSPC-4, magnification 1000×; (b) MSPC-5, magnification 1500×; (c) and (d) PE particles produced by MSPC-4, magnification 19× for (c) and 100× for (d); (e) and (f) PE particles produced by MSPC-5, magnification 19× for (e) and 101× for (f).

and replicated throughout catalyst preparation and polymerization, an important factor in relation to the possible application of such systems in gas-phase and slurry polyolefin processes. Furthermore, PE produced with MSPC-5 has a value of MWD 3.29, which is similarly regarded as the performance of single site catalyst.

In this work, PE particles produced by MSPC-5 were graded by grading sifter, and the data are listed in Table 5. It was found that nearly 95 wt.% of the PE particles, which are spherical, are concentrated in the range of $250\,\mu m < d < 850\,\mu m$, with negligible powder.

Another important feature of immobilized catalyst for olefin polymerization is to have proper catalytic life-span. In order to investigate the catalytic lifetime of MSPC-5, ethylene polymerization was conducted for 1 h. As shown in Fig. 5, though the polymerization rate gradually decreased during polymerization process, MSPC-5 exhibited considerable activity even after 1 h, indicating that a solid catalyst with satisfactory catalyst lifetime was obtained.

As indicated above, MSP-5 is a suitable and effective precatalyst for bis(phenoxy-imine) zirconium catalyst immobilization, and the method is feasible.

Table 5
The grade of PE particles produced by MSPC-5[a]

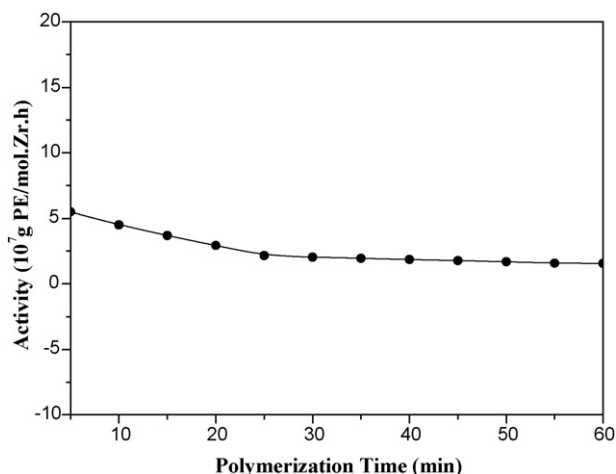| Size distribution scope	Weight percentage (wt.%)
$850\,\mu m \leq d$	0.12
$425\,\mu m \leq d < 850\,\mu m$	53.27
$250\,\mu m \leq d < 425\,\mu m$	41.58
$d < 250\,\mu m$	5.03

[a] 100 g PE particles.

Fig. 5. Kinetic profile of ethylene polymerization using MSPC-5. Polymerization conditions: 120 mg of catalyst, 3.6 mmol TEA as the scavenger and alkylating. reagent, ethylene pressure = 1.0 MPa, polymerization temperature = 80 °C, solvent = 1000 ml hexane, polymerization time = 1.0 h.

4. Conclusions

Bis(phenoxy-imine) zirconium catalyst, bis-[*N*-(3-*tert*-butylsalicylidene) cyclohexylaminato] zirconium(IV) dichloride, has been directly impregnated onto MAO modified spherical MgCl$_2$ support. It was found that the texture of support, the element on solid catalysts, the activities of the supported catalysts for ethylene polymerization and the properties of resultant polymers strongly rely on dealcoholization temperature.

Especially, MSP-5 supported bis(phenoxy-imine) zirconium catalyst not only showed high activity, but also produced spherical polymers with high bulk density, without reactor fouling. Further studies, such as the effect of polymerization conditions on the catalyst activities and the properties of polymers, are in progress.

Acknowledgement

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