

Spherical MgCl_2 -supported MAO pre-catalysts: preparation, characterization and activity in ethylene polymerization

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Abstract

The spherical magnesium chloride (MgCl_2)-supported methylaluminoxane (MAO) pre-catalysts were prepared using $\text{MgCl}_2 \cdot 2.6\text{EtOH}$ adduct as support material subjected to elimination of EtOH by thermal treatments. The pre-catalysts were characterized by X-ray diffraction (XRD), IR, ^{27}Al solid-state NMR, scanning electron microscopy (SEM) and N_2 BET surface areas. Under the activation of triethylaluminum (TEA), polymerization of ethylene were carried out by contacting supported MAO with soluble dichloro(*rac*-ethylene-bis(1-indenyl)zirconium (*rac*-Et(Ind) $_2$ ZrCl $_2$) prior to polymerization. As a result, the polymers with spherical form morphology and high bulk density (over 0.35 g/cm^3) were obtained. The addition of cross-linking agents (CAs) during the adsorption of MAO on the support (e.g. glycol, glycerol and triethanolamine) led to an increase in Al content from 3.8 to 9–12 wt.% and in the catalyst activity. The highest activity in ethylene polymerization ($3.48 \times 10^7 \text{ g polyethylene (PE)/(mol Zr h)}$) was achieved in the case of using glycerol as CA.

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1. Introduction

The catalysts for olefin polymerization derived from metallocene compounds and methylaluminoxane (MAO) have been intensively investigated in the past few years. Although, homogeneous metallocene possesses unprecedented olefin polymerization activity and selectivity, it must be heterogenized for drop-in replacement in slurry or gas-phase plant.

Silica (SiO_2) is the most employed carrier for heterogeneous metallocene catalysts [1–7], while use of magnesium chloride (MgCl_2) as carrier is not widely reported in the literature. For the lack of hydroxyls on the surface of MgCl_2 , which is different from SiO_2 , it

is difficult to support metallocenes or MAO on MgCl_2 firmly. The main synthetic routes reported in the literature for metallocenes immobilization on MgCl_2 can be generally classified according to the preparatory method of carrier as follows: direct impregnation on ball-milling anhydrous MgCl_2 [8–10]; adsorption on MgCl_2 synthesized by the reaction between dibutylmagnesium and *tert*-butyl chloride [11] or by Grignard reagent decomposition [12–14]; direct impregnation on spherical MgCl_2 prepared by de-alcoholation of $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct [15].

All these aforementioned MgCl_2 -supported metallocene catalysts need to use trialkylaluminum or MAO as co-catalyst. When trialkylaluminums were used as co-catalyst, instead of MAO, catalyst showed modest activity [8–10,12]. In the case of MAO employed as co-catalyst, catalyst activity increased

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compared to the former case, but the amount of MAO was still high ($\text{Al/Zr} > 1000$) and the problem of poor polymer morphology can not be solved because external MAO might leach some adsorbed metallocene species during the polymerization process [11,13–5].

In order to overcome above problems, we have developed a novel method for preparing spherical MgCl_2 -supported MAO pre-catalysts, in combination with metallocenes, which produced polymers with high bulk density and desired spherical morphology [16–18]. The supported pre-catalysts are prepared by immobilizing MAO on the spherical MgCl_2 only and polymerization starts immediately after contacting the pre-catalysts with soluble metallocenes, which eliminates the need for a supporting and separate step of metallocenes. No additional MAO is required, the catalytic system can be activated with common alkyl aluminum. This polymerization process is similar to that of SiO_2 in-site supported metallocene catalyst, reported by Soares and co-workers [19–21].

The spherical MgCl_2 has been the common used support in the conventional Ziegler–Natta catalysts [22,23]. But as far as we are aware, there appears to have been few reports on spherical MgCl_2 -supported MAO pre-catalysts. In this paper, we describe the preparation of the pre-catalysts and their use in the polymerization of ethylene.

2. Experimental

2.1. Materials

Solvents (*n*-hexane and toluene) and gases (ethylene and nitrogen) were purchased from commercial sources and purified according to the usual procedures. Dichloro(*rac*-ethylene-bis(1-indenyl))zirconium (*rac*-Et(Ind)₂ZrCl₂) and spherical $\text{MgCl}_2 \cdot n\text{EtOH}$ adduct ($n = 2.6$, measured by TG analysis) were donated from Brici, China. Glycol, glycerol and triethanolamine (reagent grade, Beijing Chem. Co., China) were all dried with 4 Å molecular sieve and stored under nitrogen. MAO (in toluene solution) and triethylaluminum (TEA) were purchased from Ethyl Co., USA and used without further purification. All the chemicals were manipulated in inert atmosphere using the Schlenk technique.

2.2. Support preparation

Ten grams of spherical $\text{MgCl}_2 \cdot 2.6\text{EtOH}$ adducts were heated under a stream of N_2 at 250 °C for 4 h, as a result, 4.5 g supports were obtained.

2.3. Pre-catalysts preparation

All the supported MAO pre-catalysts were prepared according to the following typical procedures.

MgCl_2/MAO : 12 ml of MAO (1.8 M toluene solution) was added to 3 g of supports in 30 ml of toluene, followed by vigorous stirring of mixture at 70 °C for 4 h. The solid part was then washed with toluene and dried in vacuum.

$\text{MgCl}_2/\text{MAO}/\text{cross-linking agent (CA)}$ (e.g. glycol, glycerol or triethanolamine): 12 ml of MAO (1.8 M toluene solution) and an appropriate amount of CAs were added to 3 g of supports in 30 ml of toluene. A mixture was vigorously stirred at 70 °C for 4 h. The solid part was then washed with toluene and dried in vacuum.

2.4. Characterization of supports and pre-catalysts

Power XRD patterns of samples were obtained with a Philips instrument, model X'Pert equipped with a source using a Cu anode, operating at 40 kV and 40 mA for Cu K α radiation. The sample was covered with an amorphous polyethylene (PE) film to avoid air contact. The diffraction pattern was recorded in the range of $10^\circ < 2\theta < 70^\circ$.

The IR spectra were recorded on the Magna-IR spectrophotometers. The samples of the support and pre-catalysts for IR examination were prepared in glove box as Nujol mulls in KBr pellets and a solid MAO sample was analyzed with infrared microscope.

The Al contents of the supported MAO pre-catalysts were determined by titrimetry, after acid extraction and by complexometry with EDTA using dithizone as indicator.

The ²⁷Al solid-state NMR spectra were recorded at 104.3 MHz on a Varian Unity Plus 400 spectrometer. The number of accumulation was ca. 5000 with a pulse width of 3 μs and 0.5 s delay between the pulses. Chemical shifts were referenced to the external 1 M aqueous solution of AlCl_3 . Prior to spectra recording,

samples were transferred in a glove box and packed into 7.0 mm diameter zirconia rotors.

Scanning electron microscopy (SEM) experiments were carried out on a Cambridge S-250 Mk3. The samples were mounted on specimen holder and coated with gold. The employed accelerating voltage was 19 kV.

The specific surface areas and the pore size distribution were measured by N_2 adsorption using the BET method with CE-Instruments Milestone 200.

2.5. Polymerization of ethylene

All polymerizations were carried out in a 21 stainless steel autoclave reactor. Prior to polymerization, the spherical $MgCl_2$ -supported MAO pre-catalyst was brought into contact with $rac\text{-Et(Ind)}_2ZrCl_2$ in toluene solution. One liter of *n*-hexane and 2 mmol of TEA were added to the reactor at room temperature under nitrogen purging, followed by the addition of mixture of supported MAO pre-catalyst and soluble metallocene. Then the reactor was heated to the polymerization temperature (80 °C). The polymerizations were started by the pressurizing of the reactor with ethylene (total pressure = 15 bar) and the polymerization temperature was maintained within ± 0 °C of the set point. The polymerizations were carried out for 1 h and then were terminated by venting the gaseous monomer, instead of by injecting some alcohols into the reactor.

2.6. Characterization of the polymers

The polymer melting points (T_m) were measured by differential scanning calorimetry (DSC) in a Perkin–Elmer DSC-7. The analyses were performed with a heating rate of 10 °C/min in the temperature range of 25–200 °C.

The bulk density of the polymer particles was measured according to ASTM Standard D 1895.

3. Results and discussion

3.1. The adsorption of MAO on $MgCl_2$

It is well known that the thermal treatment of $MgCl_2 \cdot nEtOH$ adduct with irregular morphology ob-

tained by ball-milling method at temperature of 250 °C removes EtOH completely [24]. But for spherical $MgCl_2 \cdot 2.6EtOH$ adduct in this paper, after thermal de-alcoholation, the small amounts of EtOH may be retained inside of the $MgCl_2$ support. Fig. 1 presents IR spectra recorded for alcoholate, support and pre-catalysts. IR spectrum of a $MgCl_2 \cdot 2.6EtOH$ sample (Fig. 1a) exhibits a broad band at 3400 cm^{-1} , corresponding to OH groups in EtOH and a feature peak at 1404 cm^{-1} attributable to alcoholate. After thermal de-alcoholation (Fig. 1b), the peak concerning alcoholate (1404 cm^{-1}) almost disappears, while there still is a weak peak at 3400 cm^{-1} , suggesting that EtOH was not completely removed during the thermal treatment, probably due to the entrapment within $MgCl_2$ structure.

Fig. 1c shows the IR spectra of solid MAO, in which a band at 870 cm^{-1} can be assigned to the Al–O bond [25]. After the direct adsorption of MAO on the support (Fig. 1d) or further addition of CA during the preparation of supported pre-catalyst (Fig. 1e), it is observed that the band corresponding to Al–O group is displaced at a lower frequency, showing a doublet at 810 and 720 cm^{-1} . It seems that in $MgCl_2$ /MAO pre-catalyst, the MAO is coordinated to $MgCl_2$ through oxygen to Mg^{2+} and its possible structure is shown in Fig. 3. It is worthwhile note, in Fig. 1d and e, that a tiny minority of EtOH still exists in $MgCl_2$ /MAO or $MgCl_2$ /MAO/glycerol, since the residual OH signal is observed in IR spectra of them.

The results of corresponding ^{27}Al solid-state NMR experiments are shown in Fig. 2. The chemical shift of solid MAO sample (Fig. 2a) is approximately 154 ppm, which agrees well with the literature data [26]. After the adsorption of MAO on $MgCl_2$ (Fig. 2b), the ^{27}Al NMR line shifts to higher magnetic field and the chemical shift decreases (154 \rightarrow 146 ppm). It is known that the increase of the coordination number moves the chemical shift towards higher magnetic field [27,28]. So, the above change of chemical shift shows the presence of Cl \rightarrow Al dative links (Fig. 3), which is another interaction between MAO and $MgCl_2$, besides the coordination through oxygen to Mg^{2+} (vide ante). Fig. 2c shows the ^{27}Al solid-state NMR spectrum of sample $MgCl_2$ /MAO/glycerol with 150 ppm of chemical shift and the tendency of decrease of chemical shift is not remarkable, for in

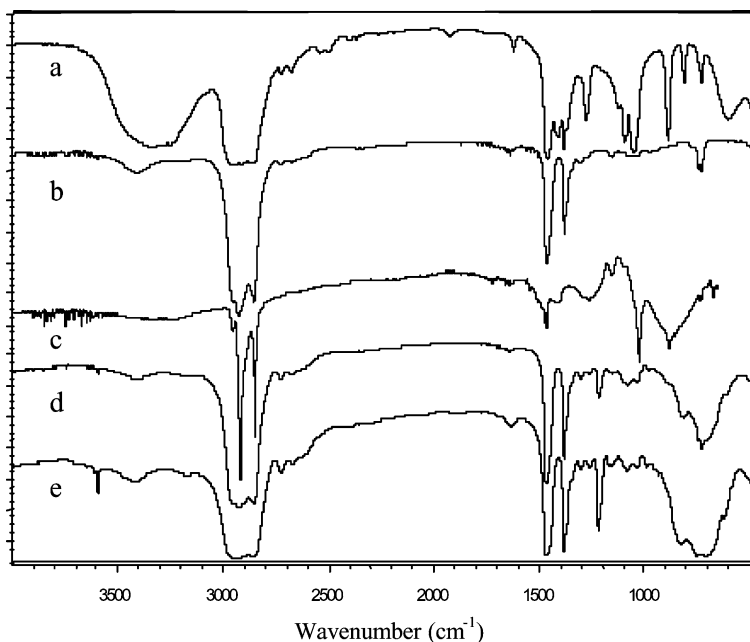


Fig. 1. IR spectra of: (a) $\text{MgCl}_2 \cdot 2.6\text{EtOH}$ adduct; (b) MgCl_2 support; (c) MAO; (d) MgCl_2/MAO ; (e) $\text{MgCl}_2/\text{MAO}/\text{glycerol}$.

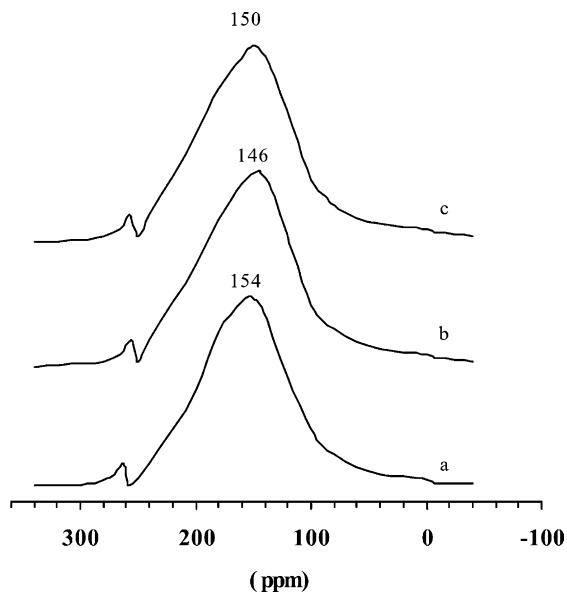


Fig. 2. ^{27}Al solid-state NMR spectra of: (a) MAO; (b) MgCl_2/MAO ; (c) $\text{MgCl}_2/\text{MAO}/\text{glycerol}$.

the sample $\text{MgCl}_2/\text{MAO}/\text{glycerol}$ some MAO is supported by the cross-linking reaction with glycerol (vide infra).

Fig. 4a is the XRD pattern of the support obtained after the elimination of EtOH, which presents reflections at $d = 1.82, 2.58, 2.94$ and 5.87 \AA related to MgCl_2 (in agreement with the literature [24]) and $d = 4.08 \text{ \AA}$ related to PE film. Fig. 4b and c show the XRD pattern of MgCl_2/MAO and $\text{MgCl}_2/\text{MAO}/\text{glycerol}$, respectively, which are both similar to that of the support (Fig. 4a).

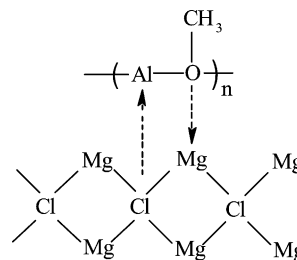


Fig. 3. A possible structure of coordination between MgCl_2 support and MAO.

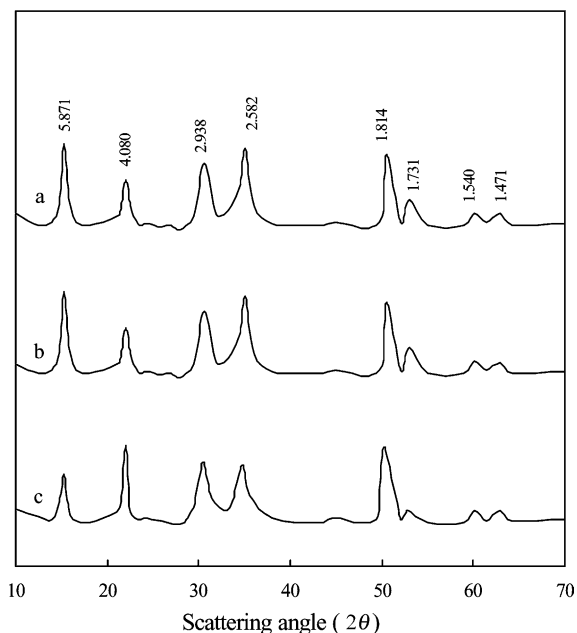


Fig. 4. XRD patterns of: (a) MgCl_2 support; (b) MgCl_2/MAO ; (c) $\text{MgCl}_2/\text{MAO}/\text{glycerol}$.

The MgCl_2/MAO pre-catalyst containing 3.8 wt.% of Al, was brought into contact with $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ and the polymerization of ethylene was initiated under the activation of TEA. The result obtained is listed in Table 1, run 1. The MgCl_2/MAO pre-catalyst demonstrates moderate activity of 1.48×10^7 g PE/(mol Zr h). Compared to analog SiO_2 -supported

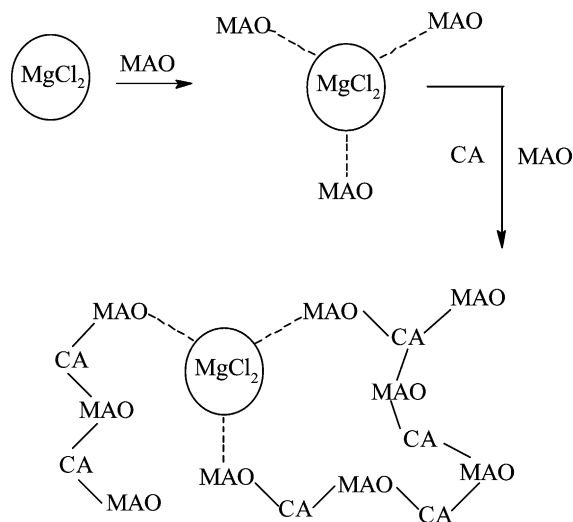


Fig. 5. The model of MAO supported on MgCl_2 through the reaction with CAs.

MAO pre-catalysts with 12 wt.% of Al and activity of 2.71×10^7 g PE/(mol Zr h) [29], the lower Al content of MgCl_2/MAO pre-catalyst give rise to the lower activity.

3.2. The effect of CAs on the properties of pre-catalyst

It has been found that MAO can react with aliphatic or aromatic diols under the evolution of

Table 1

The effect of CAs on Al contents and activity of catalyst in ethylene homopolymerization^a

Run	CA	OH/Al molar ratio ^b	Al (wt.%)	Activity (10^7 g PE/(mol Zr h))	T_m ($^\circ\text{C}$)	Bulk density (g/cm^3)
1	None	0	3.8	1.48	130.5	0.32
2	Glycol	0.2	8.5	2.10	132.0	0.35
3		0.4	12.1	2.71	131.8	0.35
4		0.6	12.4	2.33	132.1	0.36
5		Glycerol	0.1	6.8	2.95	131.5
6	0.2		9.0	3.48	131.7	0.38
7	0.4		10.1	2.72	131.1	0.37
8	Triethanolamine	0.1	7.0	1.28	132.3	0.35
9		0.2	10.4	2.04	131.2	0.36
10		0.4	11.7	1.72	131.3	0.36

^a Polymerization conditions: $p = 15$ bar; $T_p = 80$ $^\circ\text{C}$; $t_p = 1$ h; $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2 = 6.6$ μmol ; Al (MAO)/Zr = 60; Al (TEA)/Zr = 300.

^b Referred to MAO.

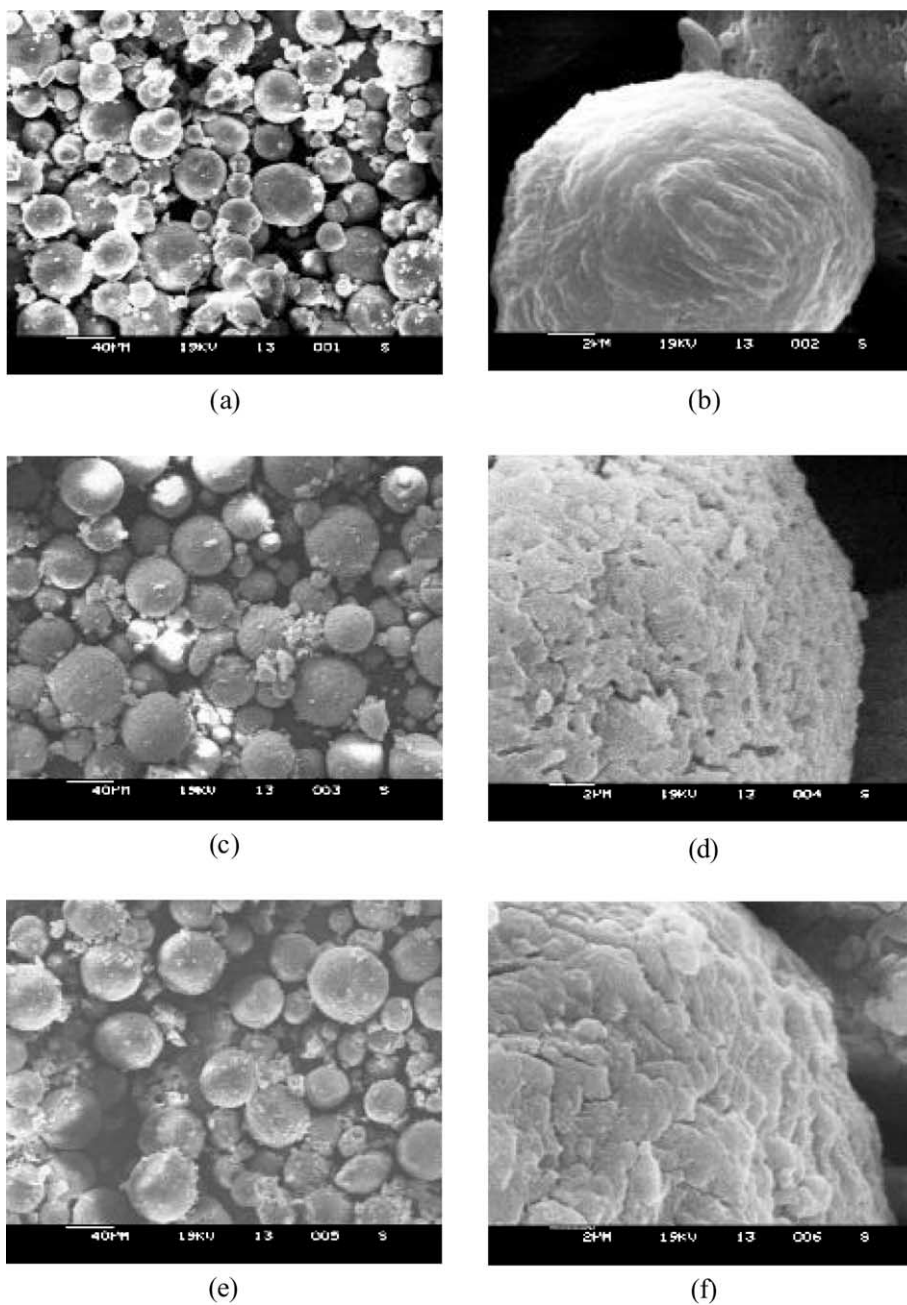


Fig. 6. SEM photographs of: (a) $\text{MgCl}_2 \cdot 2.6\text{EtOH}$ (150 \times); (b) $\text{MgCl}_2 \cdot 2.6\text{EtOH}$ (3000 \times); (c) MgCl_2 support (150 \times); (d) MgCl_2 support (3000 \times); (e) $\text{MgCl}_2/\text{MAO}/\text{glycerol}$ (150 \times); (f) $\text{MgCl}_2/\text{MAO}/\text{glycerol}$ (3000 \times).

methane gas and formation of three-dimensional lattices [30–33]. In order to increase the Al contents in the spherical MgCl_2 -supported MAO pre-catalyst, we added some CA (e.g. glycol, glycerol and triethanolamine) during the adsorption of MAO on the support. The results obtained are listed in Table 1. As the CA content added to pre-catalyst system increases, the supported Al content in pre-catalyst increases as well, suggesting that some MAO is supported through the cross-linking reaction with CA as shown in Fig. 5. But in every kind of pre-catalyst containing CA, the pre-catalyst with the highest Al content do not show the highest activity (Table 1, runs 4, 7 and 10), indicating that more addition of CA leads to uncompleted reaction in Fig. 5 and the existence of remainder hydroxyls, as a result of decrease in catalyst activity. Among three CAs, glycerol shows the highest performance and when the mole ratio of OH/Al is 0.2, the highest activity is 3.48×10^7 g PE/mol Zr h (Table 1, run 6).

3.3. The morphology, BET areas and pore volume distribution

Fig. 6 and Table 2 present the morphological and N_2 BET surface areas information during the preparation of the supported MAO pre-catalyst, respectively. The SEM photographs illustrated in Fig. 6a, c and e clearly indicate that the original spherical form of $\text{MgCl}_2 \cdot 2.6\text{C}_2\text{H}_5\text{OH}$ was kept in the MgCl_2 support and resulting $\text{MgCl}_2/\text{MAO}/\text{glycerol}$ pre-catalyst. But there are some dramatic changes on the surface appearance among $\text{MgCl}_2 \cdot 2.6\text{C}_2\text{H}_5\text{OH}$, support and pre-catalyst. The $\text{MgCl}_2 \cdot 2.6\text{C}_2\text{H}_5\text{OH}$ has a rough smooth and less porous surface (Fig. 6b), in accor-

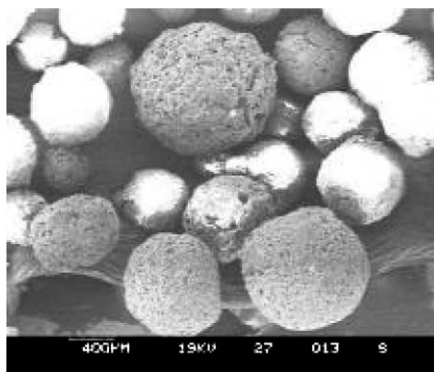


Fig. 7. SEM photographs of PE particles produced with $\text{MgCl}_2/\text{MAO}/\text{glycerol}$ and $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ (15 \times).

dance with very low surface areas and pore volume (Table 2, no. 1), while the MgCl_2 support becomes porous and loose because of elimination of $\text{C}_2\text{H}_5\text{OH}$ (Fig. 6d), in agreement with large surface areas and pore volume (Table 2, no. 2). Apparently the porous surface structure of MgCl_2 support allow complete penetration of MAO (Fig. 6f), being in favor of supporting MAO on MgCl_2 firmly and reduce the occurrence of leaching for MAO from the supported pre-catalyst.

The SEM photograph (Fig. 7) of polymers prepared with $\text{MgCl}_2/\text{MAO}/\text{glycerol}$ pre-catalyst shows that the replication of spherical catalyst morphology have been achieved successfully, indicating that the supported catalyst has a uniform distribution of active sites and high porosity [34].

Fig. 8a and b show the differential pore volume distribution of supported pre-catalysts during the preparation. It is seen from Fig. 8a that the pores with 40–60 nm diameters on the support surface are firstly filled with MAO and new pores with 120–150 nm diameters appear on MgCl_2/MAO pre-catalyst. As a result, the surface areas and pore volumes of MgCl_2/MAO pre-catalyst increase greatly compared to those of MgCl_2 support (Table 2). Fig. 8b reveals that more MAO adsorbed on the support by cross-linking reaction are filled in the pores just generated with 120–150 nm diameters. As a consequence, the surface area of the supported pre-catalyst increases further, but pore volume decreases (Table 2).

Table 2

The N_2 BET surface areas and pore volumes of $\text{MgCl}_2 \cdot 2.6\text{C}_2\text{H}_5\text{OH}$ adducts, support and pre-catalyst

No.	Samples	BET surface area (m^2/g)	Pore volume (cm^3/g)
1	$\text{MgCl}_2 \cdot 2.6\text{C}_2\text{H}_5\text{OH}$	2.14	0.03
2	MgCl_2 support	56.9	0.39
3	MgCl_2/MAO	78.5	0.45
4	$\text{MgCl}_2/\text{MAO}/\text{glycerol}$	94.7	0.25
5	$\text{MgCl}_2/\text{MAO}/\text{glycol}$	160.0	0.26

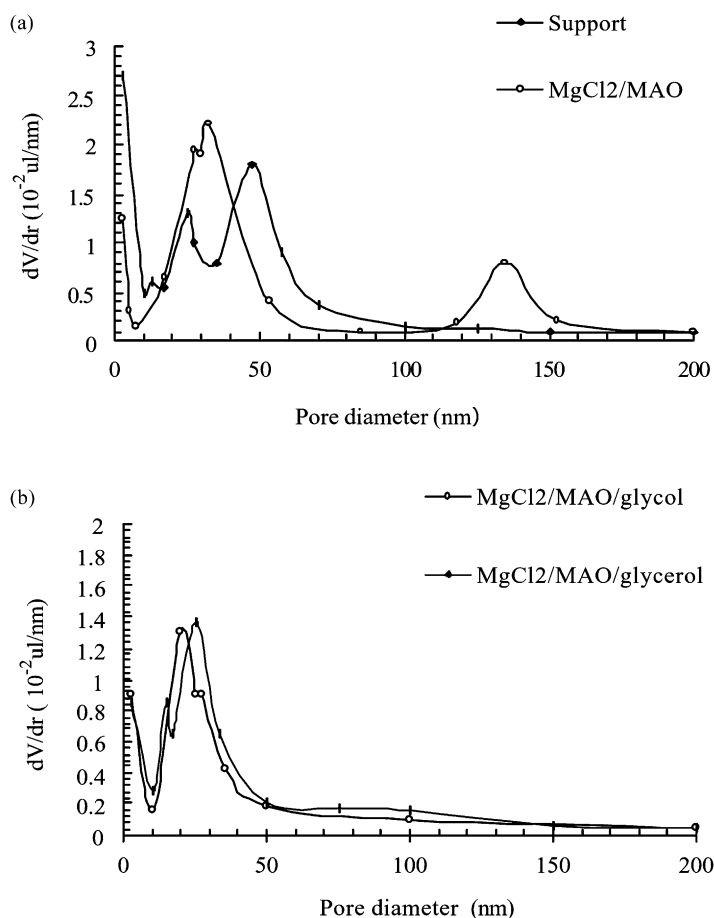


Fig. 8. The differential pore volume distribution of $MgCl_2$ support and resulting pre-catalysts.

4. Conclusions

We have developed a novel spherical $MgCl_2$ -supported MAO pre-catalyst using spherical $MgCl_2 \cdot nEtOH$ as support material. Spherical polymers with high bulk density can be produced by means of contacting supported MAO with metallocene prior to polymerization. It was found that both the Al content and catalytic activity had been greatly improved after the addition of CA (e.g. glycol, glycerol and triethanolamine) during the adsorption of MAO on support.

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