

Effect of swelling response of the support particles on ethylene polymerization

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Received 21 June 2006; received in revised form 11 September 2006; accepted 14 February 2007

Available online 20 February 2007

Dedicated to the memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

Macroporous and modified macroporous poly(styrene-*co*-methyl methacrylate-*co*-divinylbenzene) particles (m-PS and mm-PS) supported Cp_2ZrCl_2 were prepared and applied to ethylene polymerization using methylaluminoxane (MAO) as cocatalyst. The influences of the swelling response of the support particles on the catalyst loading capabilities of the supports as well as on the activities of the supported catalysts were studied. It was shown that the Zr loadings of the supports and the activities of the supported catalysts increased with the swelling extent of the support particles. The m-PS or mm-PS supported catalysts exhibited very high activities when the support particles were well swollen, whereas those catalysts devoid of swelling treatment gave much lower activities. Investigation on the distribution of the supports in the polyethylene by TEM indicated that the swelling of the support particles allowed the fragmentation of the catalyst particles. In contrast, the fragmentation of the support particles with poor swelling was hindered during ethylene polymerization.

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Keywords: Supported metallocene catalysts; Swelling; Fragmentation

1. Introduction

During the past decade there have been tremendous industrial and academic interests in the development of highly active and selective metallocene catalysts for olefin polymerization [1–6]. Practical applications have required that such homogeneous catalysts are used in heterogeneous mode by immobilizing on solid supports [7–10]. The most commonly used supports are inorganic materials, such as SiO_2 and MgCl_2 , but the applications of polymers as supports are known to be an increasingly important feature from such a viewpoint that organic carriers are readily available for use, easily

functionalized to satisfy certain requirements and well incorporated into the final polyolefin products [11–14]. Heterogeneous polymerization catalysts require well-designed support particles that are capable of undergoing fragmentation, which is necessary to maintain monomer access to catalytic active sites located within the support [15,16]. In the case of inorganic materials supported Ziegler–Natta catalysts, it is generally accepted that the catalyst particles break up into small fragments and the fragments uniformly dispersed into the polymer particles throughout the whole growth process [17–19]. A similar phenomenon has also been observed for supported metallocene catalysts on inorganic substrates, such as silica [20]. However, ordinary organic supports, mostly based on functionalized poly(styrene-*co*-divinylbenzene) resins with various content of crosslinking density, commonly have poor fragmentation abilities due to the irreversible crosslinking

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[21]. Unlike inorganic materials with rigid characteristic or loose structure, organic supports are usually of solid and flexible particles, which can only carry catalyst on their outer surface and are hindered in fragmentation during polymerization of olefins. Recently, we reported a novel method of supporting metallocene catalyst on a porous polystyrene latex [22]. The porous structure of this catalyst particle facilitates fragmentation of the support during ethylene polymerization and this technique can be well applied to the preparation of polymer blends with very fine microstructure [23]. However, this method is restricted only to those small-sized supports. Since applicable support particles should have a certain size (usually about 50 μm), a new strategy must be considered.

Generally, suspension polymerization is used to synthesize polymer particles with micrometer-size diameter. Macroporous and gel-type polystyrene (PS) particles are two representative examples [24]. If the suspension polymerization is carried out with a styrene/divinylbenzene monomer mixture containing an appropriate organic solvent (as diluent or porogen), the obtained resin is called macroporous or macroreticular PS particles (m-PS) with permanent porous structure. When the monomer mixture consists of styrene and divinylbenzene only, the product has a hard and glassy consistency, which is usually called gel-type PS particles (g-PS). Hong et al. [25] demonstrated a new simple encapsulation technique to immobilize metallocene catalysts inside the g-PS particles by swelling–shrinking characteristic of the support, because no complex chemical reactions are necessary. However, it is a potential problem of this method that the enclosed catalyst easily falls off during polymerization.

In this report, we have developed supported metallocene catalysts based on m-PS resin particles and modified macroporous crosslinked PS resin particles (mm-PS) and applied them for ethylene polymerization. It is shown that the swelling response of the organic support particles greatly influences the activities of the supported catalysts for ethylene polymerization and even the fragmentation process as frequently observed with the silica- or alumina-supported catalysts.

2. Experimental

2.1. Materials

The monomers, styrene (St), including methyl methacrylate (MMA) and divinylbenzene (DVB) were distilled at reduced pressure under a nitrogen atmosphere. The polymerization initiator, benzoyl peroxide (BPO), was purified by recrystallization with ethanol. Analytical grade dodecylbenzene sulfonic acid sodium salt (SDBS), Na_3PO_4 , CaCl_2 , NaOH and polyvinyl alcohol (PVA, average polymerization degree: 2400–2500) were used without further purification. Toluene was dried over 4 Å molecular sieves for 10 days, then refluxed over Na/K alloy for at least 8 h and distilled. Bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2 , Boulder Scientific Company), methylaluminoxane (MAO: 10 wt% in toluene, Ethyl Corporation) and ethylene (polymerization grade,

Liaoyang Chemical Corporation) were used without further treatment.

2.2. Preparation of supports

The gel-like polystyrene particles (g-PS) were made by suspension polymerization, using hydroxyapatite (HAP) and PVA as suspension stabilizers. Suspension polymerization was carried out in a three-neck reactor fitted with condenser and mechanical stirrer (600 rpm) under an argon atmosphere. The reactor was charged with 1.0 g of PVA, 120 ml of HAP solution and 180 ml of water. After stirring for 30 min, the reactor was heated to 85 °C and the polymerization was initiated by adding the comonomer and initiator mixture (18 ml of St, 2 ml of MMA, 0.5 ml of DVB and 0.05 g of BPO). After stirring for 3 h, the resultant g-PS particles were separated from the serum, washed with water and screened by wet screenings to obtain particles with diameters ranging in 60–80 μm . In the case of preparing macroporous PS particles (m-PS), additional toluene (4 ml typically, as a porogen) was added into the comonomer mixture. And modified macroporous PS particles (mm-PS) were prepared using the same procedure as m-PS besides adding SDBS (0.02 g) in the aqueous phase. Prior to use, all the PS particles were dried at 70 °C under vacuum overnight.

2.3. Preparation of supported catalysts

MAO pretreatment of the supports and the reaction between Cp_2ZrCl_2 and the supports were conducted under an argon atmosphere in a specially designed flask with a magnetic stirring bar in it. About 1.0 g of the support was first suspended in 20 ml of toluene with vigorous stirring. MAO solution (3.0 ml) in toluene was added into the suspended support mixture and stirred overnight at 55 °C. The liquid phase was removed and the solid was washed with 20 ml of toluene for four times. After the MAO treated support was suspended again in 20 ml of toluene, 20 ml of catalyst solution in toluene ($c(\text{Zr}) = 4 \text{ mmol/l}$) was added and stirred for different periods of time (1–12 days) at 60 °C. Finally, the supported catalyst was obtained by removing the liquid phase, washed four times with 20 ml of toluene, dried under vacuum at room temperature, and recovered as free flowing powder.

2.4. Polymerization of ethylene

Ethylene polymerization was performed in toluene medium in a glass reactor equipped with a mechanical stirrer. The reactor was dried and degassed thoroughly, followed by introduction of the solvent. MAO was used as cocatalyst in an Al/Zr molar ratio of 800 or 400. For each experiment, about $3 \times 10^{-5} \text{ mol/l}$ of Zr was used (40–80 mg of catalyst suspended in 150–200 ml of toluene depending on the metal loading of the support). Prior to use, the supported catalysts were dunked in toluene for different periods of swelling time (0–12 h). The catalyst and the additional MAO were mixed at room temperature for 20 min and then transferred

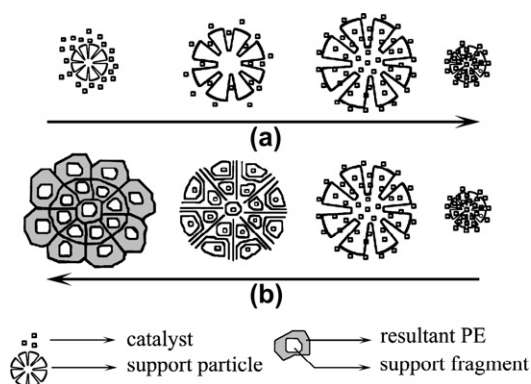
into the reactor under argon atmosphere. After the reactor was set to the required temperature (40 °C or 60 °C), the polymerization was carried out by pressurizing the reactor with ethylene for 60 min at 600 rpm. Acidified (HCl) ethanol was used to stop the polymerization. The precipitated polymer products were separated by filtration, washed with ethanol, and finally dried under reduced pressure at 60 °C overnight.

2.5. Analytical procedures

Images of the supports and polyethylene products were obtained by scanning electron microscope (SEM) using TAX-840 SEM. Information on fragmentation of the support inside polyethylene was obtained under transmission electron microscope (TEM) performed on a JEOL2010 microscope operating at 200 kV, and before observed the polyethylene product was microtomed to about 50 nm and stained for 12 h at room temperature using RuO₄. The zirconium (Zr) and aluminium (Al) loadings of the supported catalysts were measured by inductively coupled plasma atomic emission spectroscopy (Plasma-Dec (I) of America Leeman Lab.). The molecular weight and molecular weight distributions of polymers were investigated with a high temperature gel permeation chromatography (PL-GPC 220) instrument at 130 °C, using 1,2,4-trichlorobenzene as an eluent. Melting points (T_m) of the polymer products were determined by differential scanning calorimetry (DSC) performed on a Perkin–Elmer DSC-7 instrument, using a heating rate of 20 °C/min in the temperature range of 40–180 °C under nitrogen.

3. Results and discussion

Recognising that lightly crosslinked polystyrene (PS) particles can swell in some organic solvents (e.g. toluene) via creating space or ‘solvent porosity’ within the resin and allowing ready access by small molecules to the interior of the resin particles, we can exploit this swelling property to immobilize catalytic species inside the support particles as schematically presented in Scheme 1a. With increase of swelling extent of



Scheme 1. Schematic diagram for (a) the preparation of the supported metalocene catalyst via swelling–shrinking of the support particles and (b) the fragmentation of the catalyst particle in ethylene polymerization through the swelling response of the support particle.

the PS particles, more metallocene complex molecules are capable of accessing the interior of the particle and anchored by carbonyl group on the PS particles. After dried, the PS particles shrink. During polymerization process, with increase of swelling extent of the supported catalyst particles, more olefin monomers are capable of accessing the catalytic sites inside the supports and being polymerized therein, especially in the well swollen state of the catalyst particle, resulting in fragmentation of the support particles due to the mechanical stress from formation of a lot of the polyolefin chains inside the pores (Scheme 1b). Therefore, by improving the swelling ability of the support, more catalytic species will be evenly distributed throughout the support particles and the resultant catalyst particles will be more easily fragmented during olefin polymerization. This idea leads to more simple, practical, effective and economical method for the preparation of polymer supported metallocene catalysts.

The PS support particles with macroporous structure (m-PS) and those with loose structure (mm-PS) shown in Fig. 1 were targeted. By making the support particles with macroporous or loose structure we could improve their swelling abilities in toluene. All of the supports were prepared via suspension copolymerization using St, MMA and DVB as comonomers. Here MMA monomer was inserted into the resin particles to provide coordination sites for anchoring catalyst. The swelling abilities of the support particles were detected by dipping them in toluene for long enough time (4 days), and then some particles were put on a hot stage to be observed using a Leica DMLP microscope and the images at swollen state were recorded right now. After that, the particles on hot stage were heated to 140 °C and held at this temperature for 1 h to get rid of solvent thoroughly, the images of dry state were obtained. The results showed that the m-PS and the mm-PS resin particles had excellent swelling response, and the diameter of the former increased to about 1.25 times of the original particle and that of the latter to about 1.5 times in diameter (Fig. 2). On the contrary, the g-PS possessed so poor swelling ability and its diameter had little change during the same dipping process.

The support particles obtained were used for immobilizing Cp₂ZrCl₂ as metallocene catalyst. The immobilization was done noncovalently, analogous to modified silica supports. Cp₂ZrCl₂ was supported on the mm-PS, m-PS and g-PS particles through different stirring time in toluene, leading to various Zr loadings of the supports. This allowed us to investigate the influence of the swelling response of the support particles on the metal loading capacity of the supports. Fig. 3a shows the Zr loadings as a function of supporting time for the three types of the support particles, from which we observed that the metal loadings increased with the swelling response of the support particles. The Zr loading on the g-PS support was quite lower (less than 0.4 mg-Zr/g-support) due to the dense structure which resulted from limited swelling ability and obstructed the catalyst components to be immobilized into the interior of the support particles. In the case of the mm-PS and m-PS supports, the Zr loadings were not high at the beginning, perhaps confined to the outer layer of the support particles,

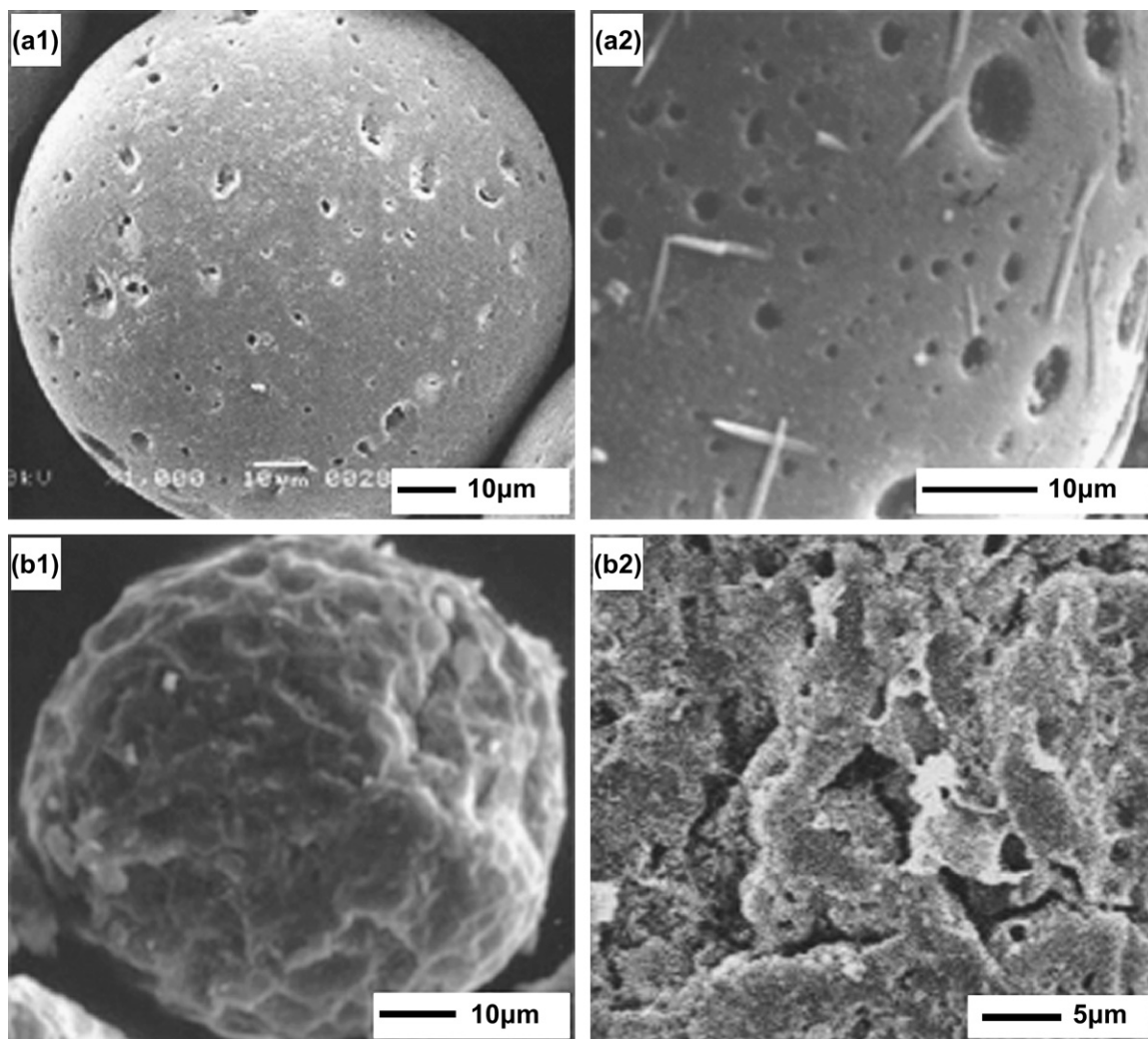


Fig. 1. SEM images of the m-PS support particle (a1) and its surface (a2), and the mm-PS support particle (b1) and its surface (b2).

until a long enough time when the supports were swollen sufficiently to allow diffusion of catalyst components into the support interior. A high loading was achieved after supporting time of 4 days. The mm-PS support showed high efficiency in Zr loading with the maximum of 14 mg-Zr/g-support because of its superior swelling ability. The m-PS support had the moderate Zr loading capability, giving a maximum of 5 mg-Zr/g-support.

The supported catalysts obtained were used to catalyze ethylene polymerization in toluene, using MAO as cocatalyst. Prior to use, the supported catalyst was firstly dipped in toluene for periods between a few minutes and 12 h, allowing the support particles to swell up to various extent. The importance of the swelling response of the support particles to the activity of the supported catalyst thus could be demonstrated by arranging an array of polymerizations with the same catalyst but different in swelling time. It was shown that the activities of the mm-PS and m-PS supported catalysts strongly depended on the swelling time, namely, the swelling response of the support particles. Fig. 3b shows the catalytic activities of the three

types of the supported catalysts for ethylene polymerization. The g-PS supported catalyst and the m-PS or mm-PS supported catalyst devoid of swelling treatment gave much lower activities, perhaps access of ethylene monomer was confined to the outer layer of the supported catalyst particles and the polymerization took place only at the outer surface. However, the activities of the m-PS and mm-PS supported catalysts increased markedly with the swelling time. Higher activity was achieved after 6 h of swelling. When the support particles were sufficiently swollen (after 9 h of swelling), the supported catalysts exhibited very high activities, producing close to 3.6×10^6 g-polymer/(mol-Zr h atm) for the m-PS supported catalyst and 3.2×10^6 g-polymer/(mol-Zr h atm) for the mm-PS supported catalyst. It was believed that the swollen support particles fragmented gradually as ethylene polymerization proceeded and the fragmentation provided more and more access to the inner active sites for the monomer. Time-dependent catalytic activities shown in Fig. 4 proved this viewpoint. The experiment was carried out at 50 °C with the m-PS supported catalyst swelled for just 2 h before polymerization, in this

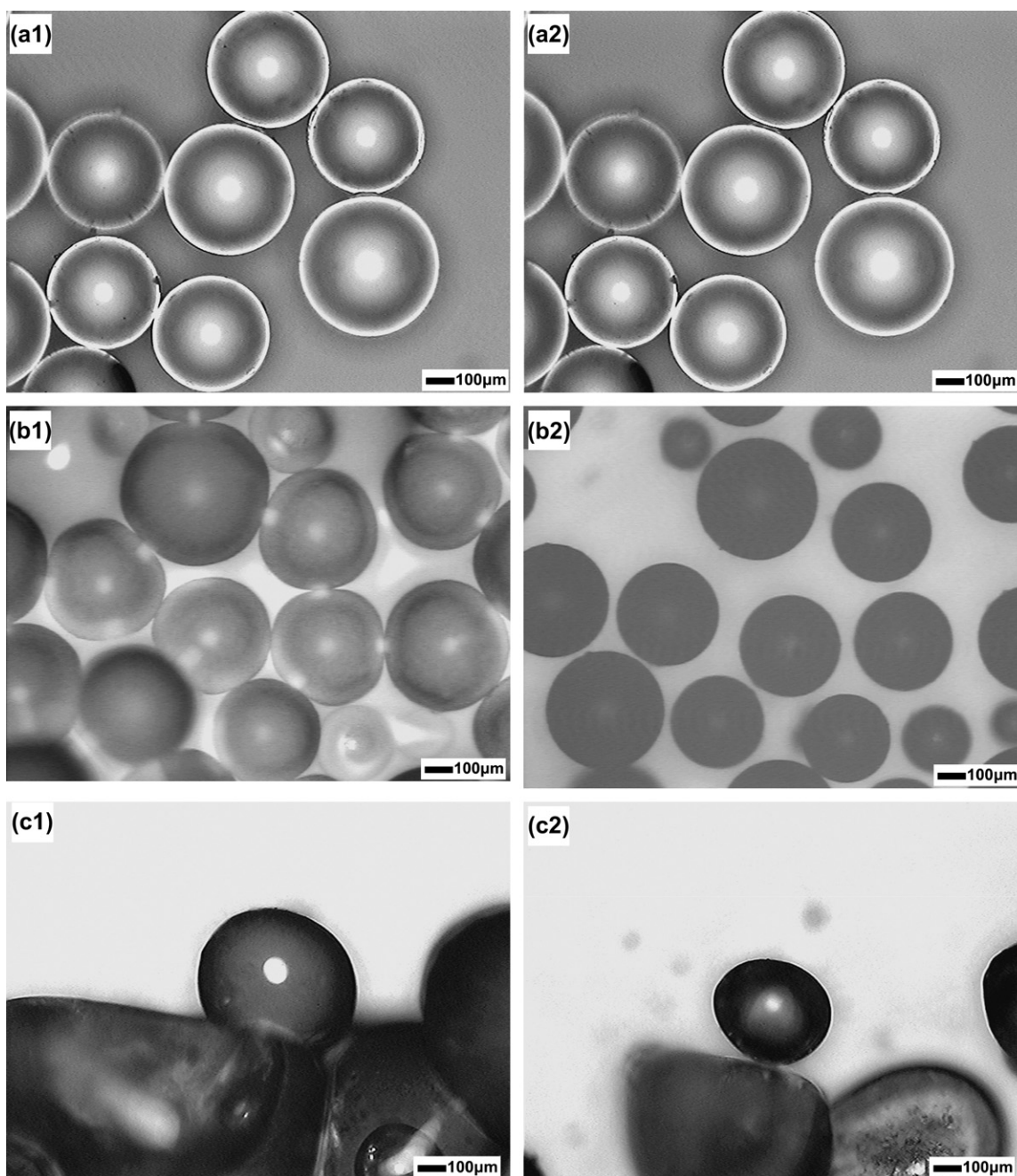


Fig. 2. The change in particle sizes of g-PS, m-PS and mm-PS supports after swelling. (a1) Swollen state of g-PS; (a2) dry state of g-PS; (b1) swollen state of m-PS; (b2) dry state of m-PS; (c1) swollen state of mm-PS; (c2) dry state of mm-PS.

case, the supported catalyst particles had not swollen thoroughly and only little ethylene diffused into the interior of the supported catalyst at the beginning of polymerization. Through such a way, time-dependent activity profile was obtained. First the swollen m-PS supported catalyst exhibited high activity during initial 10 min. A sudden drop in polymerization activity resulted from the formation of a surface covering consisted of polyethylene (PE) film that hindered a substantial diffusion of monomer. With ongoing polymerization a shell-by-shell like fragmentation of the support material

from the particle surface towards the center occurred, driven by the hydraulic force of new polymer, which was similar to the reported results [26,27]. This fragmentation released more and more active sites; hence, the macroscopic polymerization rate rose. In this way the overall activities of the supported catalysts are higher than those of unfragmentable supported catalysts.

To confirm the fragmentation of the support particles, polyethylene (PE) films were prepared in a hot press. The support particles were visible in the films when the PE was produced

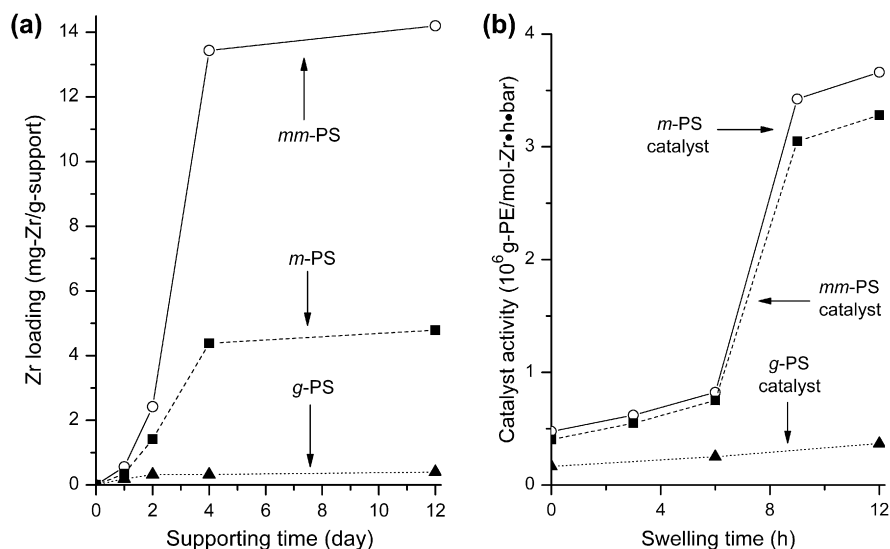


Fig. 3. (a) Effects of supporting time on Zr loading of the supports; (b) relationship of the catalyst activity of Cp_2ZrCl_2 supported on the mm-PS, m-PS and g-PS support with swelling time of the corresponding support particles. (Ethylene polymerization conditions: MAO (Al/Zr = 800) as cocatalyst, 3×10^{-5} mol/l of Zr in toluene (150–200 ml), 1.2 atm of ethylene pressure, 60 °C, 60 min.)

with the g-PS supported catalyst, or from the m-PS or mm-PS supported catalyst devoid of swelling treatment (Fig. 5a), suggesting that the support particles remain unfragmented or fragmented slightly during ethylene polymerization. In the case of the films from the PE produced with the m-PS or mm-PS supported catalysts in which the support particles were sufficiently swollen, however, no intact support particles were observed, implying that the support particles might have undergone fragmentation. Further investigation into the distribution of the support fragments in PE matrix was carried out by means of transmission electron microscopy (TEM) (Fig. 5b). It is shown that the support particles had been disintegrated into pieces and the fragments were dispersed into the PE product. Therefore, this experiment verified that the swelling of the support particles was necessary to fragmentate the catalyst particles during ethylene polymerization; otherwise, it would remain unfragmented if the support particles were not well swollen.

Due to the high activity of m-PS or mm-PS supported catalyst after swelling for 12 h, we did a series of experiments to investigate the effects of other conditions on ethylene polymerization, and it was found that the activity of m-PS or mm-PS supported catalyst also strongly depended on the amount of MAO (MAO/Zr ratio) and the polymerization temperature. The effects of polymerization temperature and MAO/Zr ratio are shown in Table 1. Increasing the temperatures from 40 °C to 60 °C or enhancing the MAO/Zr ratios from 400 to 800 led to higher catalytic activities.

However, higher activity did not always accompany with good product morphology. Morphologies of the polymers resulting from m-PS and mm-PS supported catalysts were investigated by means of SEM. The polymer particles derived from experiments at lower polymerization temperature (40 °C) were spherical and 0.3–0.6 mm in size (Fig. 6). It was well

established that the morphology of the polymer product frequently duplicated that of the catalyst particle in heterogeneous Ziegler–Natta systems [28,29] as well as in metallocene catalysts supported on inorganic substrates, such as SiO_2 . The experimental results were consistent with this phenomenon since the product with isolated particles was achieved. It was found in the experiment that either increasing the polymerization temperature or enhancing the amount of the cocatalyst brought a higher catalytic activity of the catalyst but led to a poor morphology of the resulting PE. The particles of the product became smaller and of ill-defined shapes, accompanied by a drastic reduction of bulk density. It seemed that more rapid and uncontrolled fragmentation of the active catalyst particle occurred and the formation of coherent polymer particles was prevented. This is typical of the fragmentation process of supported catalyst, and it is possible to improve

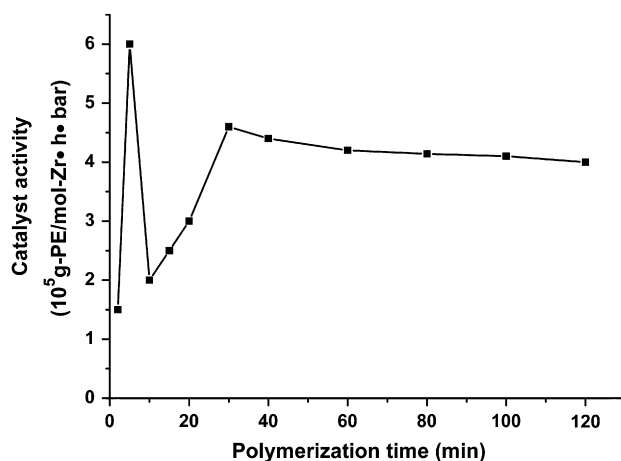


Fig. 4. Catalytic activity–time profile for ethylene polymerization with m-PS supported metallocene catalyst.

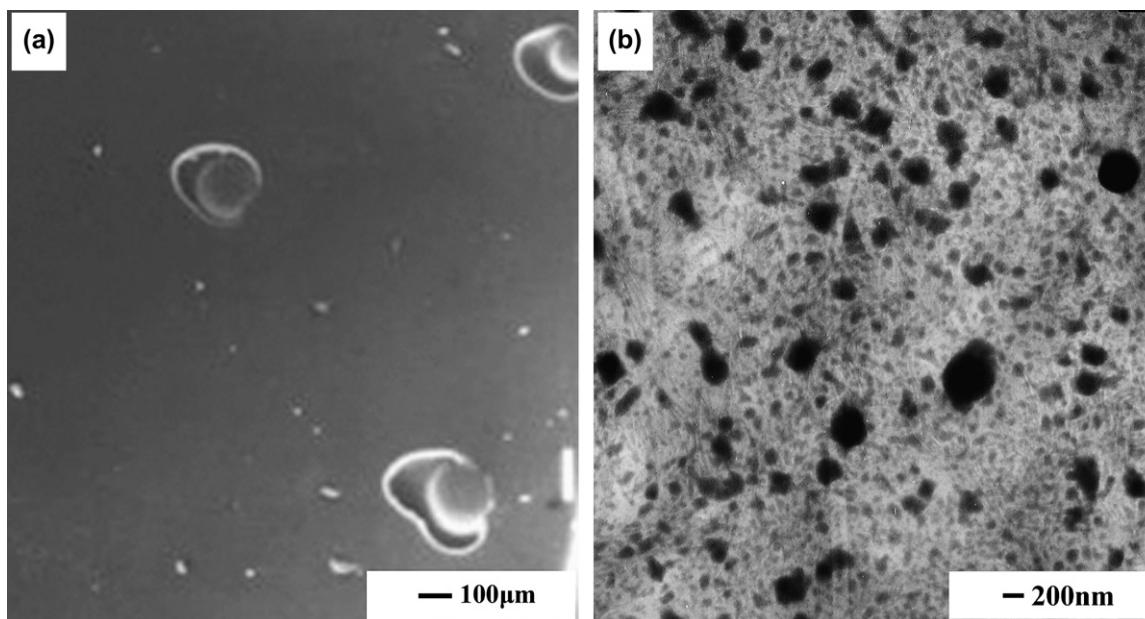


Fig. 5. (a) SEM image of the unfragmented support particles in the film from polyethylene produced with the m-PS supported catalyst devoid of swelling treatment. (b) TEM image of the support fragments in polyethylene obtained with sufficiently swollen m-PS particles supported catalyst.

Table 1

Ethylene polymerization results with m-PS or mm-PS particles supported $\text{Cp}_2\text{ZrCl}_2^a$

Run no. ^b	Cat. Inject. (mg)	Activation ^c (Al/Zr)	Polym. Temp. (°C)	Yield (g)	Activity (kg/mol h atm)	Product (g/g h atm)
1	83	400	40	7.1	1360	71
2	78	800	40	10.8	2200	115
3	84	400	60	11.3	2139	112
4	72	800	60	16.5	3644	191
5	44	400	40	11.3	1399	218
6	41	800	40	15.7	2050	319
7	42	400	60	16.0	2038	317
8	38	800	60	23.2	3268	509

^a Polymerization conditions: toluene as the dispersion solvent, 150 ml for runs 2–7, and 200 ml for runs 8–13; 1.2 atm of ethylene pressure; 60 min. All of the support particles were swollen by dipping them in toluene for 12 h.

^b Runs 1–4 were performed with m-PS supported catalyst (Zr loading of 4.78 mg-Zr/g), and runs 5–8 with mm-PS supported catalyst (Zr loading of 14.2 mg-Zr/g).

^c The Al/Zr ratios are the sum of the Al loading on the support plus the Al used in the polymerization.

the morphologies of the polymer product by varying the conditions of ethylene polymerization and the structures of the support particles.

The properties of PE obtained from ethylene polymerizations are presented in Table 2. When the polymerization temperature was raised, the molecular weight decreased remarkably as expected since the rate of chain termination (β -elimination) or chain transfer increased much faster than that of chain propagation with the increase of polymerization temperature. The melting point of the products also slightly decreased with increasing polymerization temperature. Larger amount of MAO added to supported catalyst increased the activity but had a little effect on the molecular weight and the melting temperature of PE obtained. The polydispersity of molecular weight of PE in the range of 2.5–3.0 is relatively narrow as compared with that obtained from other PS particles supported metallocene catalysts [30], implying that the

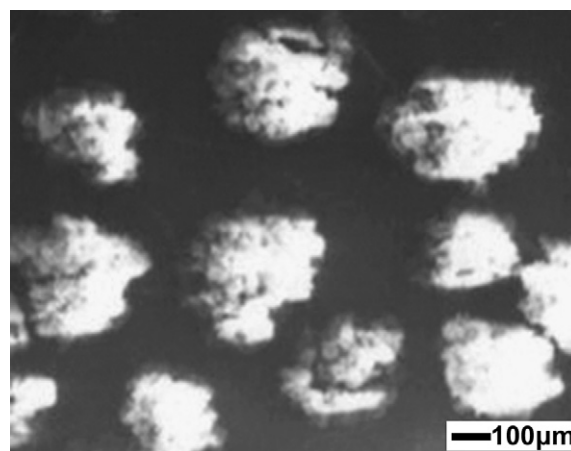


Fig. 6. SEM image of the polyethylene particles from experiment 1 mentioned in Table 1.

Table 2
Properties of polyethylene samples obtained in polymerizations mentioned in Table 1

Run no.	Polym. Temp. (°C)	M_n (kg/mol)	M_w/M_n	T_m (°C)	Bulk density (g/ml)
1	40	64.4	2.71	138.2	0.22
2	40	57.0	2.70	138.5	0.21
3	60	30.8	3.00	136.4	0.14
4	60	24.7	2.60	134.8	0.12
5	40	92.7	2.85	137.7	0.20
6	40	79.7	2.54	136.6	0.17
7	60	34.2	2.96	135.3	0.12
8	60	39.4	2.51	135.0	0.11

noncovalently immobilizing of Zr to the supports basically retains the characteristic of homogeneous metallocene catalysts.

4. Conclusion

In summary, the results described here on PS-based particles supported metallocene catalysts highlight a strategy for noncovalently immobilizing catalyst throughout the whole support particle, and importantly demonstrate that the fragmentation of catalyst particles and the activities of the supported catalysts can be controlled during ethylene polymerization via the swelling response of the support. There is considerable potential for extending this approach to different cases of chemical reaction related to polymer supports. The effect of fragmentation on the shape and morphology of growing PE particles is now in further research and will be reported in due course.

Acknowledgements

The Ministry of Science and Technology of China (Project No. 2005CB623800) and National Natural Science Foundation (Project Nos. 50525311 and 50621302) of China are thanked for financial support.

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