# Control of polymer particle size by supported metallocene catalysts

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By utilizing a pre-mixing method, we can prepare a supported metallocene catalyst producing a polyethylene of larger granular size and containing fewer fine particles than that prepared by the conventional adsorption of metallocene on a MAO-coated $SiO_2$ surface. Such supported catalyst helps to eliminate the reactor fouling during polymerization of ethylene.

**Keywords:** metallocene, supported, methylalumoxane, polymerization, ethylene

## 1. Introduction

Metallocene catalysts containing groups IVB or VB transition metal centers, especially those of Zr, Ti, or Hf, are very active in polymerization of $\alpha$-olefins producing polyolefins with narrow molecular weight distribution and specific stereochemistry [1]. They are regarded as the next generation of polymerization catalysts. However, polyethylene and polypropylene produced by homogeneous metallocene catalysts form on the reactor wall surface as sticky polymer films, which hinders the transfer of heat released by the polymerization reaction [2]. This phenomenon is called reactor fouling. Moreover, polyolefins produced homogeneously have an irregular morphology and very low bulk density (0.08 g/ml).

To solve these problems, it is necessary to anchor the metallocene onto a porous support as a heterogeneous catalyst. This approach is utilized in the present large-scale industrial production [3]. For example, the gas phase polymerization of ethylene in the commercial Unipol process was conducted in a fluidized-bed reactor utilizing a supported Ti catalyst. The polyethylene produced by such catalyst has a granular morphology and a high bulk density, and contains very few fine particles.

The present development of the supported metallocene catalyst has mainly involved the adsorption of metallocene on a methylalumoxane-coated support material such as silica, alumina, and $MgCl_2$ (adsorption method) [4–6]. The method can produce a catalyst with a satisfactory polymerization activity, product morphology and bulk density. Nevertheless, it still suffers from producing too many fine particles in the polymer product [7]. This difficulty can be overcome by prepolymerizing the catalyst with the olefin monomer at a lower temperature to increase its size prior to the polymerization reaction [3,7].

In this paper, we want to report a method for preparing a supported metallocene, which could produce directly a large granular polyethylene containing very few fine particles. To prepare such a supported metallocene catalyst, two criteria must be met. Firstly, the metallocene and MAO have to be pre-mixed to form a certain activated metallocene species for anchoring onto a support surface. Secondly, the Al content supplied by MAO should be about 30 wt% by weight of the supported catalyst (pre-mixing method).

## 2. Experimental

### 2.1. Catalyst preparation

All the preparations were under $N_2$ atmosphere. Catalysts A was prepared as follows: To a MAO/toluene solution containing 34.3 mmol of Al, 0.101 g of $(n\text{-}C_4Cp)_2$ $ZrCl_2$ (0.250 mmol of Zr) was added and reacted at room temperature for 1 h. This MAO/metallocene solution was added slowly to a toluene suspension solution containing 2.0 g at 250 °C dehydrated $SiO_2$. The mixture reacted at room temperature until its dark-red color disappeared. The liquid phase was removed and the solid residue was washed with toluene at 60 °C. The solid catalyst was dried under reduced pressure until it was free-flowing. The elemental analysis indicated that the catalyst contained 30.8 wt% Al and 1.09 wt% Zr. Catalysts B and C were prepared similarly using different amounts of metallocene and MAO.

For comparison purpose, two other catalysts were prepared using adsorption of $(n\text{-}C_4Cp)_2ZrCl_2$ onto a MAO-coated $SiO_2$, which was prepared by contacting an appropriate amount of MAO with a toluene suspension containing $SiO_2$ followed by washing, filtering, and drying [4]. A $(n\text{-}C_4Cp)_2ZrCl_2$ solution was then reacted with the MAO-coated $SiO_2$ in toluene to make catalyst D and the finished catalyst contained 1.0 wt% Zr and 21.0 wt% Al. A high-temperature vacuum treatment during the preparation of MAO-coated $SiO_2$ was reported to be beneficial for better fixing MAO onto the $SiO_2$ support [2]. A supported metallocene utilizing such support is more active and produces polymer with better morphology. The MAO-coated $SiO_2$ used in preparing catalyst E has been heated to 200 °C

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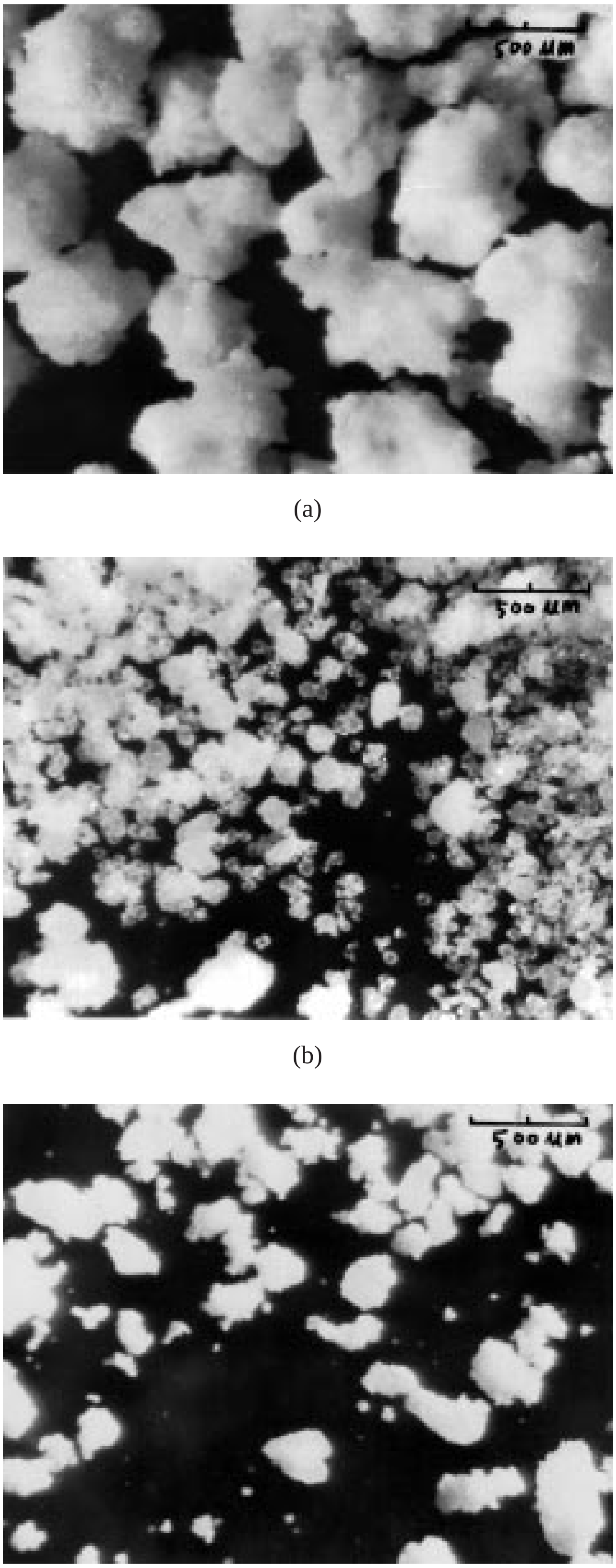
Table 1
Polymerization of ethylene over supported $(n\text{-}C_4Cp)_2ZrCl_2$ catalysts.[a]

| Catalyst | Al (wt%) | Zr (wt%) | Activity (kg-PE/g-Zr h) | Bulk density (g/ml) | % of particle $<105$ μm |
|---|---|---|---|---|---|
| A | 30.8 | 1.09 | 70.8 | 0.28 | 3.7 |
| B | 19.8 | 0.83 | 148 | 0.28 | 16.1 |
| C | 15.3 | 0.62 | 96.8 | 0.26 | 19.4 |
| D | 21.0 | 1.0 | 176 | 0.29 | 40.0 |
| E | 29.5 | 1.16 | 86.8 | 0.23 | 34.4 |

[a] Polymerization condition: 30 mg of catalyst, ethylene pressure = 10.2 atm, 5 mmol TIBA scavenger, polymerization time = 1.0 h. The melting point of all the polyethylene samples is close to 135 °C.



(a)

(b)

(c)

Figure 1. Images of polyethylene produced by supported metallocenes by different preparation methods: (a) by pre-mixing method (catalyst A), (b) by adsorption method (catalyst D), (c) by adsorption method plus vacuum/heat treatment (catalyst E).

under vacuum for 2.0 h. The composition of catalyst E is 29.5 wt% in Al and 1.16 wt% in Zr.

### 2.2. The catalyst testing and analytical procedures

The polymerization of ethylene was performed at 80 °C with 10.2 atm of ethylene pressure in a Ziper–Clave reactor using an isoparaffinic solvent, ISOPAR E. Prior to reaction, the reactor was dried by heating in vacuum and purged with $N_2$ a few times. 5 mmol of tri-*tert*-butyl alumina (TIBA) was added as the moisture and oxygen scavenger. About 30 mg of the supported catalyst suspended in the solvent was injected into the reactor through a syringe needle. When the reaction mixture reached 80 °C, the reactor was pressurized and the polymerization was initiated and continued for 1.0 h. At the end of the reaction, the ethylene pressure was released and isopropanol was added to decompose the unreacted catalyst and TIBA. The granular polyethylene was separated from the reaction mixture by filtration and dried overnight in a 110 °C oven. The results of the polymerization reaction are summarized in table 1.

The portion of polyethylene particles smaller than 105 μm was estimated by the Coulter light scattering method. A Wild M3 light microscope equipped with a Polaroid camera revealed the morphology of polyethylene. The elemental analysis was performed with an ICP-AES on digested catalysts. The melting temperature of the polyethylene was measured by differential scanning calorimetry.

## 3. Results and discussion

Although the polyethylenes obtained with the pre-mixing and adsorption methods have the same melting point of 135 °C, they display a significant difference in product morphology and the number of fine particles in the final product, as depicted in figure 1. The polyethylene particles in figure 1(a) were produced by a pre-mixing catalyst (catalyst A). They have a granular morphology with very few fine particles and their medium size is about 450 μm. Particle size analysis indicated that only 3.7% of them have diameters smaller than 105 μm. Figure 1(b) displays polyethylene particles produced by using the adsorption method (catalyst D). It obviously contained many small particles with a size around 50 μm. Although the larger polyethylene particles are granular, many small ones duplicate the spherical shape of the $SiO_2$ support [3]. The fraction of these particles with size smaller than 105 $\mu$m is 40%. Catalyst E, prepared by the adsorption method plus heat/vacuum treatment, produced polyethylene with particles size between catalysts A and D. The medium particle was about 250 $\mu$m (figure 1(c)). Nevertheless, 34% of them still is smaller than 105 $\mu$m. The morphology of these polymer particles was granular but the degree of irregularity was higher comparing to those produced using catalyst A.

It was clear that with the similar MAO content (similar Al wt%), catalysts prepared by the pre-mixing method generally produced significantly less fine particles than those prepared by the adsorption method. As can be seen in table 1, catalyst A produced less fine particles than catalyst E (3.7 vs. 34.4%) and catalyst B produced less than catalyst D (16.1 vs. 40.0%). However, among catalysts produced by the premixing method, the number of fine particles in the polyethylene decreased with increasing MAO content in the catalyst. Catalyst C, containing 15.3 wt% Al, produced a polyethylene with 19.4% fine particles. In contrast, catalyst A, containing twice the amount of MAO (Al = 30.8 wt%), produced only 3.7% fine particles.

It needs to be pointed out that a higher MAO content in a supported metallocene catalyst is not the only requirement to meet in order to lower the number of fine particles in the polyethylene. Catalyst E, prepared by the adsorption method and containing 29.5 wt% Al, still produced a polyethylene with 34.4% fine particles. We have to adopt simultaneously the pre-mixing of metallocene and MAO and use enough MAO to achieve 30 wt% Al loading in order to reduce the number of fine particles to the minimum. The bulk densities of all polyethylene samples produced by both methods (0.23–0.29 g/ml) were much higher than those produced by homogeneous metallocenes (0.08 g/ml).

The polymerization activities provide an interesting insight in the nature of the active sites of these two types of supported catalysts. With similar MAO content, the activities of catalysts prepared by the adsorption method were higher than those prepared by the pre-mixing method. For example, catalyst D (21% Al) has an activity of 176 kg/g-Zr h comparing to that of catalyst B (19.8% Al) of 148 kg/g-Zr h. Catalyst E (29.5% Al) with an activity of 86.8 kg/g-Zr h is more active than catalyst A (30.8% Al) which has an activity of 70.8 kg/g-Zr h. The activities of pre-mixing catalysts increase with the MAO content up to around 20 wt% of Al. This trend is similar to those observed with the homogeneous metallocene catalysts where the system with a higher Al/Zr mole ratio usually is more reactive [8]. However, further increase in Al wt% results in reduction of the polymerization activity (70.8 kg/g-Zr h for catalyst A). Such reduction of activity seems to relate to the fact that an excessive amount of MAO cocatalyst in the pre-mixing solution leads to the formation of less active metallocene species [9].

The distinct difference in polymerization activity and product morphology suggests that the active sites in these two types of supported metallocenes are clearly different. In the adsorption method, the $(n\text{-}C_4Cp)_2ZrCl_2$ was methylated directly by MAO already anchored on the $SiO_2$. The resulting $[(n\text{-}C_4Cp)_2ZrCH_3]^+$ was fixed onto the $SiO_2$ surface through the ion pair interaction using MAO-coated $SiO_2$ as the counter ion, and served as polymerization active sites [4,5]. In the pre-mixing method, with a large excess of MAO in the pre-mixing solution, the methylated metallocene species, $[(n\text{-}C_4Cp)_2ZrCH_3]^+[MAO]^-$, undertook further $\alpha$-hydrogen transfer reaction with MAO to produce a $[Zr–CH_2–Al]$ species and methane according to Kaminsky [9]. Such $[Zr–CH_2–Al]$ species had been found less reactive for polymerization of olefins [9]. The species was then adsorbed onto the $SiO_2$ surface similar to that of binding MAO to the $SiO_2$ surface [4–6] and served as the active sites for polymerization in the pre-mixing catalysts. Thus, the supported catalysts prepared by the pre-mixing method were lower in polymerization activity than those prepared by the adsorption method.

## 4. Conclusions

Supported metallocene catalysts prepared by a conventional adsorption method produced a polyethylene with a wide particle size distribution and an undesirable amount of fine particles. We had found that using a pre-mixing solution of a higher MAO content, we could prepare a supported metallocene catalyst, which produced directly a large granular polyethylene powder containing very few fine particles. The significant difference in polyethylene morphology and the polymerization activity clearly indicated that these two preparation methods created different active metallocene species on the surfaces of the supported catalysts.

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