

## Spatial distribution of active Ti species on morphology controlled Mg(OEt)<sub>2</sub>-based Ziegler-Natta catalyst

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### ABSTRACT

Though Ziegler-Natta catalysts for propylene polymerization prepared by spherical Mg(OEt)<sub>2</sub> precursor have been shown high performances for industrial application, it's still uncertain how the performances originate. In this paper, effects of preparation method on particle morphology were investigated in comparison of Mg(OEt)<sub>2</sub>-based catalyst with MgCl<sub>2</sub> grinding one. The particle morphology and the polymer growth are different between the catalysts mainly due to the difference of the spatial Ti distribution in the particles. Mg(OEt)<sub>2</sub>-based catalyst has uniform spatial distribution of active Ti species over the catalyst particles, leading to well-controlled initial fragmentation and subsequent homogenous polymer particle growth.

**KEYWORDS:** MgCl<sub>2</sub> supported Ziegler-Natta catalyst, catalyst preparation method, Mg(OEt)<sub>2</sub> precursor, particle morphology, Ti distribution

### INTRODUCTION

Polypropylene (PP) produced by Ziegler-Natta (ZN) catalyst has achieved one of the highest level of industrial chemical productions, that is over forty million tons per year. Great improvements of the performance of ZN catalysts have been regarded as the main reason, accomplished through the development and optimization of catalyst components as well as the

synthetic route to the final catalyst. The most important direction of catalyst development has been to find new donor compounds for improving the stereospecificity and to establish well-defined catalyst preparation methods including the use of various starting materials [1, 2]. In the industrial aspect, particle morphology, relating to the morphology of catalyst particles through replica phenomena, has been widely investigated, which strongly affects control of kinetic behavior and the productivity of polyolefin processes (formation of fine and agglomerated particles, bulk density and etc.) as well as excellent processing properties of final polymer powders [1-4]. Thus, understanding and controlling particle morphologies and their polymer growth is an interesting and practical issue.

A number of previous investigations of the kinetic and morphological aspects of olefin polymerization with ZN catalysts have investigated and reported the importance of the early stage of polymerization and fragmentation [3, 5-9]. The whole image for the polymer particle growth has been also described by solid core model [10], polymer flow model [11], more sophisticated multi grain model [12, 13] etc. [14]. However, it is not sufficiently understand with regard to separation of chemical and physical effects, relationship between reaction condition and particle properties etc. [2, 15]. Thus, the control of catalyst particle is necessary to get more clear insight relating to morphological study, which affects the catalytic performance such as polymerization kinetics and polymer properties produced.

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The wide range of catalytic performances was affected by catalyst preparation method. The preparation methods of  $\text{MgCl}_2$ -based ZN catalysts are typically classified grinding method using  $\text{MgCl}_2$  and chemical method using  $\text{Mg}(\text{OEt})_2$  as a starting material. Spherical  $\text{Mg}(\text{OEt})_2$ -based catalyst prepared by chemical method are known to be the most advanced industrial catalyst [16], which shows the highest level of catalytic ability, including good particle replication. The catalyst becomes gradually and widely used in the industrial applications. Nevertheless, despite the interesting properties and importance for present and future industrial, limited number of studies focused on this catalyst system have been reported [17-20]. Effects of these catalyst preparation methods on the catalyst performance have been reported [21, 22]. They studied differences in the kinetics among different preparation methods. The catalyst made by grinding method showed relatively higher initial activity with fast decay having irregular shapes and sizes of polymer particle, while chemically made catalyst exhibited relatively slow activation with long-standing activity, leading to better polymer morphology. And it was confirmed by scanning Auger electron microscopy [23] and X-ray photoelectron spectroscopy [24] that the degree of the localization of Ti species on the particle surface was affected by the preparation procedures.

Even there are some studies about kinetics and some characterization as mentioned above,  $\text{Mg}(\text{OEt})_2$ -based catalyst focused on the morphological study has been scarcely investigated. It is still unclear the origin, why and how  $\text{Mg}(\text{OEt})_2$ -based catalyst shows high performance with good morphology.

In this study, effects of preparation methods were investigated on particle morphology and their evolution by means of direct SEM observation compared between basic and advanced supported ZN catalysts. It was found that the  $\text{Mg}(\text{OEt})_2$ -based catalyst makes the polymer with good morphology. While, the grinding catalyst led to poor particle morphology. The catalyst preparation methods was found to affect their distribution of Ti species in the particle to control the initial fragmentation and growth of the polymer particles.

## EXPERIMENTAL

### Materials

Propylene of research grade (donated by Japan Polypropylene Co., Ltd.), nitrogen, anhydrous  $\text{MgCl}_2$  (specific surface area of  $65.1 \cdot \text{m}^2 \cdot \text{g}^{-1}$ , donated by Toho Titanium Co., Ltd.), anhydrous and spherical  $\text{Mg}(\text{OEt})_2$  (average particle size of  $28.5 \mu\text{m}$ ),  $\text{TiCl}_4$ , and triisobutylaluminium (TIBA, donated by Tosoh FineChem Co., Ltd.) were used without further purification. Ethylbenzoate (EB) as an internal donor, *n*-heptane and toluene were used after dehydration with the molecular sieve 4A.

### Catalysts preparation

Two types of supported ZN catalysts were used in this study. These catalysts were synthesized based on the following methods.

#### i) Chemical reaction method (Cat-C)

Cat-C was also prepared based on the patent with slight modification [16]. Dropwisely 80 ml of  $\text{TiCl}_4$  was added into 240 ml of toluene slurry containing 40 g of  $\text{Mg}(\text{OEt})_2$ , and then gradually heated up to  $90^\circ\text{C}$ . After the addition of 12 ml of EB, the mixture was kept at  $90^\circ\text{C}$  for 2 h. The obtained solid was washed with toluene, additionally treated with 80 ml of  $\text{TiCl}_4$  and toluene 200 ml at  $90^\circ\text{C}$  for 2 h, and washed with *n*-heptane.

#### ii) Grinding method (Cat-G)

Cat-G was prepared according to the previously reported method [25]. Briefly, 36 g of  $\text{MgCl}_2$  and 7.8 ml of EB in a 1.2 L stainless steel vibration mill pot with 55 balls were ground for 24 h at r.t. The ground powder was then stirred with 200 ml of  $\text{TiCl}_4$  at  $90^\circ\text{C}$  in a 1 L three-necked flask for 2 h, followed by washing with *n*-heptane.

The catalysts compositions prepared by the two kinds of methods are shown in Table 1.

### Polymerization

Propylene slurry polymerizations at both atmospheric and middle pressure were carried out based on the following procedure. In 1 L stainless steel reactor equipped with magnetic stirrer, 500 ml of *n*-heptane,  $1.0 \times 10^{-3}$  mol of TIBA as cocatalyst were injected into a reactor under nitrogen. After flowing propylene for 1 h at  $30^\circ\text{C}$ , measured amounts of catalyst corresponding to

**Table 1.** Characterization of the two kinds of catalysts.

Catalyst	Ti <sup>a)</sup> (wt.-%)	EB <sup>b)</sup> (wt.-%)	Average particle size <sup>c)</sup> ( $\mu\text{m}$ )
Cat-C	3.28	15.4	28.0
Cat-G	1.83	11.2	21.8

<sup>a)</sup>determined by titration.

<sup>b)</sup>determined by gas chromatography.

<sup>c)</sup>determined by particle size distribution analysis.

Al/Ti molar ratio 100 were introduced in the order to start propylene polymerization. Propylene was continuously introduced to keep desired pressure during polymerization. Polymerization was terminated after 1 h by adding ethanol.

### SEM and PSD analyses

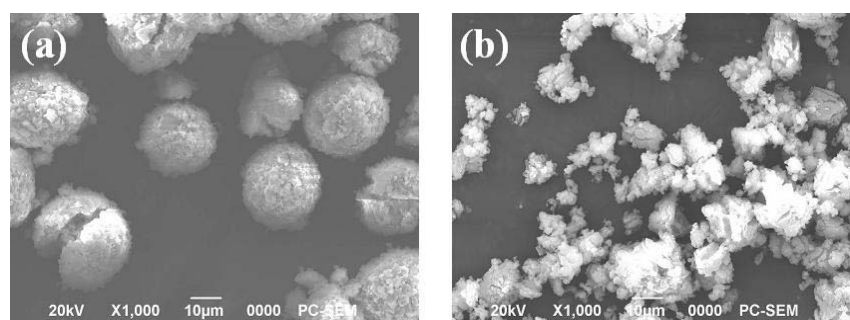
The catalysts and PP particles obtained were analyzed using SEM (JEOL JSM-6390). The particle size distribution (PSD) of catalyst as well as PP was obtained using a laser diffraction particle size analyzer (HORIBA LA-920 for catalyst, Sympatec HELOS & RODOS for PP).

## RESULTS AND DISCUSSION

The catalyst particle of Cat-C prepared using  $\text{Mg}(\text{OEt})_2$  as a starting material was characterized by SEM and PSD together with  $\text{MgCl}_2$ -based Cat-G. SEM images and the PSD were shown in Figures 1 and 2, respectively. Cat-C mainly showed spherical shapes, indicating good replication of the spherical  $\text{Mg}(\text{OEt})_2$  particles (Figure 1(a)). On the other hand, most of the catalyst particles of Cat-G have irregular shapes with fine and

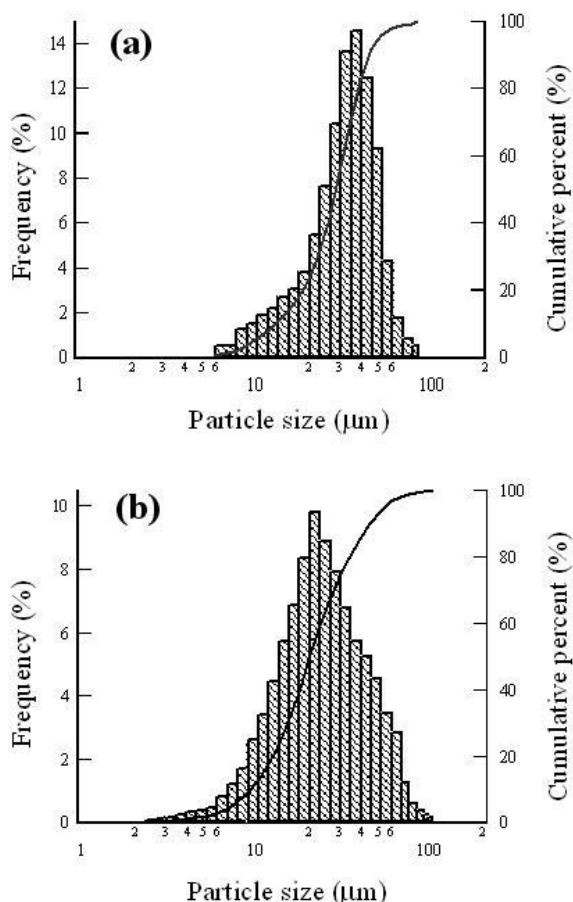
agglomerated particles, which must be due to the severe physical ball milling process of the original  $\text{MgCl}_2$  particles (Figure 1(b)). As a result of feature of the obtained particles, the catalysts have different PSD patterns; a narrow PSD for the Cat-C centered at *ca* 30  $\mu\text{m}$ , in contrast to a highly broad PSD for Cat-G centered at *ca* 20  $\mu\text{m}$ . The PSD of the original  $\text{Mg}(\text{OEt})_2$  precursors had a similar broadness with the corresponding catalyst centered at 26–27  $\mu\text{m}$ , indicating good replication of the spherical  $\text{Mg}(\text{OEt})_2$  particles as was also confirmed by SEM observations for Cat-C.

The catalysts were used for propylene slurry polymerization at an atmospheric pressure. Figure 3 shows the obtained PP particles morphology. The particle shapes for Cat-C basically replicate the shape of the original them. Especially most of the polymer particles have spherical shapes for Cat-C in Figure 3(a). The SEM image for the polymer particles produced using Cat-G shown in Figure 3(b) reveals poor particle morphology including irregular shapes and fine particles, which look similar to the morphology of the original catalyst. However, the size of fine particles was smaller considering the growth rate of average particle size. It indicates that the smaller them were made by not original fine particles, but fragmentation of growing particles while the polymerization proceeds because of severe fragmentation to cause separation of the catalyst particles into finer particles. The PSDs of PPs have same trend with that of catalysts; the PP for Cat-C has relatively narrower range of size, while broader was observed for Cat-G. These results indicate that the final polymer morphology seems to relate with not only catalyst morphology



**Figure 1.** SEM images of the original catalyst particles. (a): Cat-C and (b): Cat-G.

but also polymerization rate, especially at the initial stage. The higher polymerization rate, namely higher activity at initial stage, attributes to rapid and high growth rate of polymer. When particle

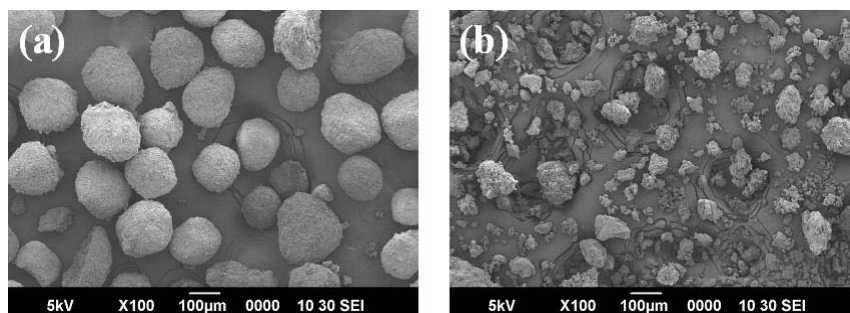


**Figure 2.** PSDs of the original catalyst particles. (a): Cat-C and (b): Cat-G.

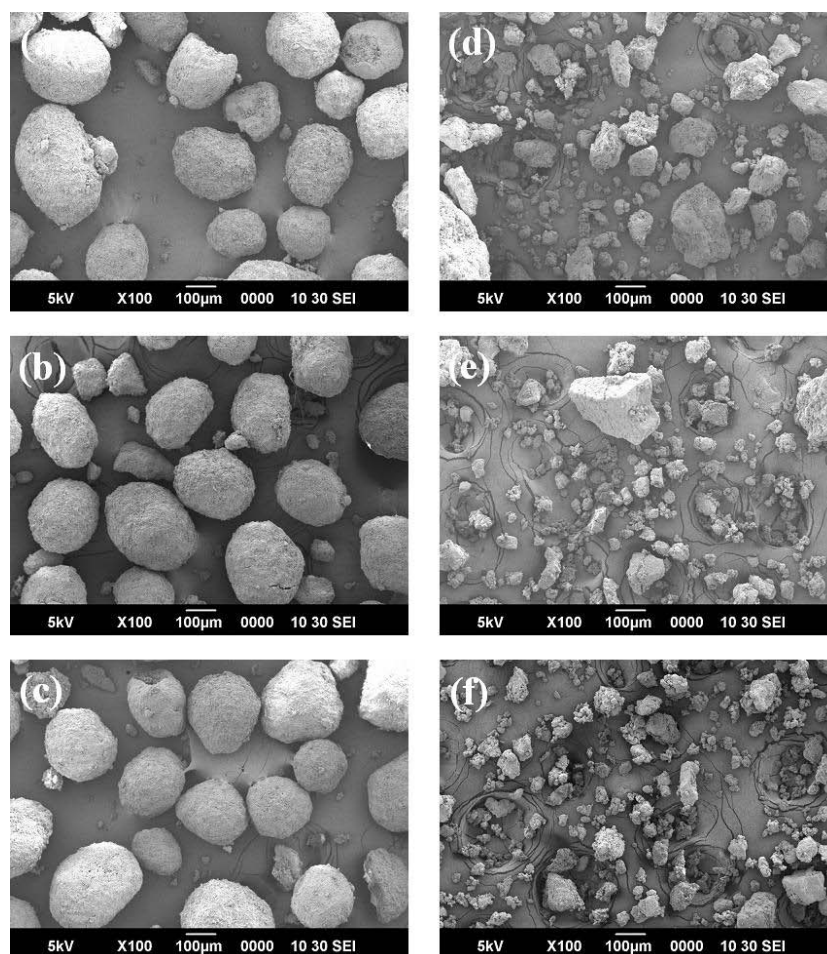
strength of catalyst is not enough to keep replicated toward growth rate of polymer, the particle morphology of total polymer would collapse.

Slurry polymerization at higher pressure (up to 0.7 MPa) was conducted to investigate why the morphology evolution mentioned above is different between the catalysts. Three levels of polymerization pressure were used in this study. The particle morphology of obtained PPs at three pressure conditions were shown in Figure 4. The particle morphology of polymer keeps constant as replicated original catalyst for Cat-C, even polymerization pressure is elevated (Figure 4 (a)-(c)). And the particle size was observed to increase gradually with the polymerization pressure. For Cat-G, the particle morphology was similar with at atmospheric pressure including fine and agglomerated ones, and the size of the particle seems to increase a little with polymerization pressure (Figure 4 (d)-(f)). These results imply that the difference of morphology evolution is affected by the distribution of polymer growth rate in the particle, namely the distribution of active species for polymerization.

There is possible explanation of the differences of the morphology evolution between the catalysts, which suggests the distribution of active Ti species in the catalyst particle. Considering that catalyst was not preliminary contacted with cocatalyst in this polymerization condition, Ti species on the outermost surface of catalyst particles mainly contributes to polymerization at the beginning [20, 25], presumably due to the diffusion effect of the cocatalyst into the catalyst particle [26]. Based on the SEM results that the differences of particle



**Figure 3.** SEM images of PP particles obtained by atmospheric pressure condition. (a): Cat-G and (b): Cat-C.



**Figure 4.** SEM images of PP particles obtained by three levels of pressure condition. (a): Cat-C (0.30 MPa), (b): Cat-C (0.50 MPa), (c): Cat-C (0.70 MPa), (d) Cat-G (0.30 MPa), (e): Cat-G (0.50 MPa), and (f): Cat-G (0.70 MPa).

morphology of PPs is caused by varying the rate of the fragmentation between the catalysts, the fact that Cat-G showed severe fragmentation to cause separation of the particles into finer particles than that of Cat-C suggested that large amounts of active Ti species for polymerization could reside on the outermost surfaces of the catalyst particles rather than inside [20, 25], since the grinding process hardly reconstructs the bulk part of the original  $\text{MgCl}_2$  particles and  $\text{TiCl}_4$  is supposed to be attached only to the surface of the fractured  $\text{MgCl}_2$  particles [27]. Considering that Cat-C has higher Ti content in catalyst than Cat-G (Table 1), therefore, the Ti species are relatively dispersed into the whole particle for Cat-C, leading to mild initial activity with long-standing activity and homogenous particle growth to obtain well-controlled good

morphology, while they are relatively localized on the outermost surface for Cat-G, leading to high initial activity and poor particle morphology. This is consistent with the previously reported polymerization kinetics [21, 22], which correlated with a decay-type kinetics for Cat-G and with a build-up-type kinetics for Cat-C.

## CONCLUSION

Morphological study on the most advanced industrial olefin polymerization catalyst,  $\text{Mg}(\text{OEt})_2$ -based catalyst, was conducted for propylene polymerization. SEM and PSD results demonstrated good replicated morphology by homogenous growth of the polymer particles, in contrast to the severe fragmentation and extensive PSD broadening of PP obtained by the  $\text{MgCl}_2$

ground catalyst. The preparation methods affect the spatial distribution of active Ti species in the catalyst particle, leading to different initial growth rate of polymer. Therefore, the origin of the high performance of the Mg(OEt)<sub>2</sub>-based catalyst is explained by uniform spatial distribution of active Ti species in all over the catalyst particles to successfully control the initial fragmentation process and subsequent stable growth of the polymer particles. Control of the spatial distribution of active Ti species in the catalyst particles is very important and useful for the establishment of well-designed catalyst particle to supply higher activity and efficient process productivity.

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