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Kinetic and Morphological Investigation on the Magnesium Ethoxide-Based Ziegler-Natta Catalyst for Propylene Polymerization Using Typical External Donors

Ali Dashti,[1] *S.A. Ahmad Ramazani,*[1] *Yuichi Hiraoka,*[2,3] *Sang Yull Kim,*[2,4]
Toshiaki Taniike,[2] *Minoru Terano**[2]

Summary: Kinetic and morphological aspects of slurry propylene polymerization using a $MgCl_2$-supported Ziegler-Natta catalyst synthesized from a $Mg(OEt)_2$ precursor in the presence and absence of two different external donors are investigated. The kinetic profiles show similar trend in presence and absence of donors. The $Mg(OEt)_2$-based catalyst show a mild activation and a long-standing activity with good replication of the catalyst particles. The results show that synthesized $Mg(OEt)_2$-based Ziegler-Natta catalyst presents a highly stable polymerization activity and good replication due to the uniform Ti distribution all over the catalyst particles.

Keywords: external donor; kinetics; morphology; $Mg(OEt)_2$-based; Ziegler-Natta propylene polymerization

Introduction

Polyethylene (PE) and polypropylene (PP) and their copolymers share more than 50% of the total worldwide polymer production. Although it is possible to produce these polymers with both Ziegler-Natta (ZN) and metallocene catalyst systems, due to some technical and economical restrictions for metallocene catalyst systems, still heterogeneous ZN catalysts is the main route to response to the strong demand of polyolefin market which is still growing significantly, especially for PP. Typical propylene polymerization ZN catalysts are titanium tetrachloride supported on a magnesium dichloride ($TiCl_4/MgCl_2$) combined with internal and external donors. The last two components are added to mainly improve the stereospecificity of the produced polypropylene. These catalysts can be used in bulk, slurry, and gas phase propylene polymerization processes, where the kinetic behavior and morphological development of propylene polymerization is one of the most important issues. In general, the kinetic behavior of polymerization with a moderate initial activity followed by a slow decay rate of the catalyst activity is practically efficient to produce desirable particle morphology and also to control reactor performance and conditions in polymerization process.[1–6] ZN catalysts synthesized from spherical $Mg(OEt)_2$ solid precursors[7] are known to show the highest level of the performance, that is good replication and highly stable activity. It has been widely used in the world industrial processes over the world in competition with alcohol adduct-based spherical catalysts. As presented by Tait et al.[8] and confirmed in our previous study[9] the

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[1] Chemical Engineering and Petroleum Department, Sharif University of Technology, P.O. Box 11155/9465, Tehran, Iran
[2] School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan
Fax: 81 761 51 1625;
E-mail: terano@jaist.ac.jp
[3] Yuki Gosei Kogyo Co., Japan
[4] Samsung Total Petrochemicals Co., Korea

$Mg(OEt)_2$-based catalyst exhibited the highest overall activity in spite of the low initial activity, since it had the largest number of active sites. In fact, The $Mg(OEt)_2$-based catalyst show a mild activation and a long-standing activity with good replication of the catalyst particles. The observed kinetic profile is discussed in relation to spatial distribution of $TiCl_4$ on the outermost of and inside of the catalyst particles.[9] Furthermore, the morphology of powder particles, which is related to the morphology of catalyst particles through replication phenomena are discussed. However, it has been known that the addition of external donors to catalyst system is essential to keep the catalyst isospecificity for propylene polymerization, as well as to get appropriate particle morphology.[10] Further, the presence of external donors in propylene polymerization generally affects the kinetic profile.[8,10,11] Thus, investigation of the effect of the absence and presence of external donors in polymerization system on kinetic behavior as well as catalyst/polymer particle morphology and their relation has been an interesting and practical issue.

In this study, we have investigated kinetic and morphological features of propylene polymerization using a $Mg(OEt)_2$-based ZN catalyst in the absence and the presence of two different external donors including ethylbenzoate (EB) and cyclohexylmethyl- dimethoxysilane known as C-donor. The two types of external donors demonstrated similar trend in the kinetic polymerization profiles in comparison with the polymerization in the absence of external donor. However, the EB as an external donor showed the higher activity and stereospecificity than the C-donor as external donor. The $Mg(OEt)_2$-based ZN catalyst showed a typical build-up type kinetics with good polymer morphology developments confirmed with scanning electron microscopy (SEM) and particle size distribution (PSD). Both the stable kinetics and good replication behaviors of the $Mg(OEt)_2$-based ZN catalyst were regarded to originate from the uniform spatial dispersion of active sites in catalyst particles.

Experimental Part

Materials

Propylene of research grade (donated by Japan Polypropylene Co.), nitrogen, $TiCl_4$ and triisobutyl aluminum (TiBA, donated by Tosoh Finechem Co.) were used without further purification. ethylbenzoate (EB) was used as internal and external donors after dehydration with 13X molecular sieves. cyclohexylmethyldimethoxysilane known as C-donor was supplied commercially. Heptane and toluene were purified by passing through a column with molecular sieves 4A. Anhydrous spherical $Mg(OEt)_2$ was from Yuki Gosei Kogyo Co.

Catalysts Synthesis and Polymerization

A $Mg(OEt)_2$-based $TiCl_4/EB/MgCl_2$ catalyst was prepared based on the patent[7] with slight modifications presented in our previous work.[9] The final catalyst called Cat-C with Ti content of 3.3 wt% and average particle size of 28.0 μm.

The slurry polymerization of propylene was carried out using the procedure mentioned in the previous paper.[9]

^{13}C-NMR Spectroscopy

The mesopentad fraction was measured by ^{13}C-NMR (Varian Gemini-300) at 120 °C with hexachloro-1,3-butadiene as a diluent and 1,1,2,2-tetrachloroethane-d_2 for the internal lock and internal chemical shift reference.

SEM and PSD Analysis

The catalyst and obtained polymer particles were analyzed by scanning electron microscopy (SEM, JEOL JSM-6390). The catalyst particle size distributions (PSD) were obtained by a laser diffraction particle size analyzer (HORIBA LA-920). The PSDs of the obtained polymers were directly measured from SEM pictures in a statistical way to study the morphology developments for the polymerization time.

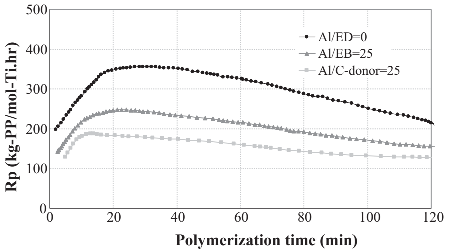

Figure 1.
Kinetic profiles of propylene polymerization.

Results and Discussion

Kinetic Profiles in the Absence and Presence of two External Donors

In Figure 1, the kinetic profiles of propylene polymerization in the absence and presence of the two external donors including EB and C-donor are demonstrated for the Cat-C. As shown in Figure 1, the trends of the kinetic profiles were similar with and without EB and C-donor as external donors, while the total activity were lowered in the presence of EB and C-donor. However, using EB as external donor shows quite higher activity than the C-donor as external donor in the same Al/ED molar ratio. The kinetics for the Cat-C belonged to the build-up type with a slow activation rate followed by a relatively long stationary period for 2 h.

Table 1 summarizes some useful parameters to quantitatively evaluate the kinetic curves of the Cat-C, where the initial rate and decay indices were respectively defined as $(dR_p/dt)_0$ and $R_p(max)/R_p(2\,h)$. The addition of EB as an external donor more or less decelerated the decay rates with a decrease in the averaged instantaneous consumptions (equal to the activities) by 24–32%. In the presence of C-donor, the averaged instantaneous activities decreased by 46–52%. Furthermore, the EB as external donor showed higher isospecificity of final polymer with higher *mmmm%* than the C-donor as external donor in the same conditions.

SEM and PSD of Catalyst/Polymer Particles

The kinetic profile obtained by using the $Mg(OEt)_2$-based ZN catalyst showed considerable differences with other conventional ZN catalysts.[8,9] Our recent results with the stopped flow technique[12–15] that the nature of active sites was almost similar for the ball milled and $Mg(OEt)_2$-based catalysts indicate the kinetic difference may arise from other factors such as spatial distribution of Ti active sites on the catalyst surface, morphology and particle size distribution of catalyst particles.[16] Thus, morphological studies of catalyst and polymer particles to evaluate the effects of these factors on kinetic behaviors have been useful.

The original catalyst particles were characterized with SEM and PSD. Figure 2 shows the SEM image of the Cat-C. Most of the catalyst particles of the Cat-C possess spherical shapes, indicating good replication of the spherical $Mg(OEt)_2$

Table 1.
Kinetic and analytical results of propylene polymerization

	Cat-C		
External donor	no	EB	C-donor
$R^a_{p,ave}$ (kg-PP/mol-Ti·h)	345	237	158
$R^a_{p,max}$ (kg-PP/mol-Ti·h)	360	248	188
$(\text{Decay index})^a_{ave}$	1.65	1.60	1.47
Initial rate index^a	11.0	10.9	14.9
mmmm^c (mol%)	56	75	72

^{a}Averaged and maximum instantaneous consumptions of propylene.
^{b}Defined as $R_p(max)/R_p(2\,h)$ and $(dR_p/dt)_o$.
^{c}Determined by ^{13}C-NMR.

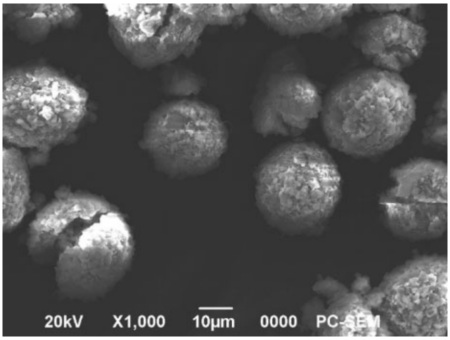

Figure 2.
SEM image of original catalyst particles of the Cat-C.

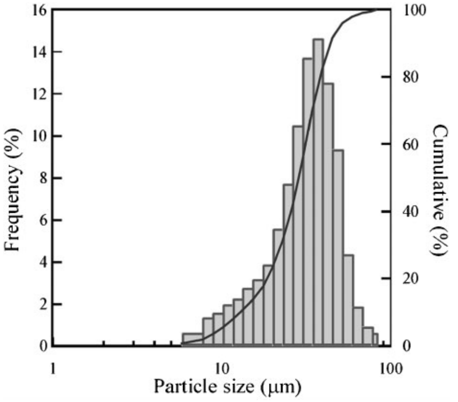

Figure 3.
Original particle size distribution of Cat-C.

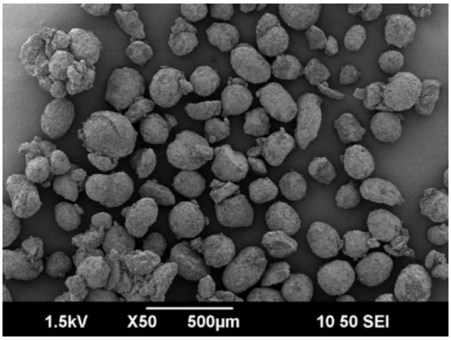

Figure 4.
SEM image of PP particle.

particles. It is notable that a few particles (the left-bottom corner of Figure 2) showed a cracked structure keeping a spherical shape, which might happen during the reaction of $TiCl_4$ with the $Mg(OEt)_2$ precursor.

The PSD analysis of the Cat-C is shown in Figure 3. As was deduced from the SEM image in Figure 2, the $Mg(OEt)_2$-based catalyst exhibited narrow particle size distribution centered at *ca.* 30 μm. The PSD of the original $Mg(OEt)_2$ precursors had a similar wideness centered at 26–27 μm, indicating good replication of the spherical $Mg(OEt)_2$ particles as was also confirmed in the SEM.

Next, the morphology development of the produced polymer particles at different polymerization stages in the presence of EB as an external donor was acquired with SEM. Figure 4 shows typical SEM image of the polymer particles produced by the polymerization using Cat-C for 90 min with EB as an external donor. It should be mentioned that the SEM image in the Figure 4 is only a part of the whole SEM image in the different polymerization time, but it was confirmed the same trend in the other cases.

As can be seen in Figure 4, most of the polymer particles have spherical shape, replicating the shape of Cat-C in Figure 2. A few particles have non-spherical shapes, such as agglomerated or broken ones. A plausible origin to cause such the unfavorable event might be the fracture of the original catalyst particles that was occasionally found in the SEM image of Figure 2 (the left-bottom corner). At the early stage of the polymerization, the rapid growth of polymer inside catalyst pores generally forms a tension.[6] This tensile force might overcome the strength of the fractured parts in order to separate them into some irregular particles.

In order to examine the morphology development of the polymer particles for the Cat-C, the PSDs of the polymer particles were statistically analyzed based on the SEM images at different polymerization times, where the number of sampling was typically over 200 polymer particles for each plot. Different polymerization times were selected regarding to the individual kinetic profile; 15, 45, 90 and 120 min (see Figure 1).

Figure 5 shows the PSD evaluation for the Cat-C. The PSD was acquired from a

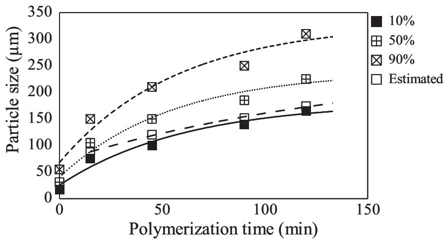

Figure 5.
Evaluation of polymer particle size at different polymerization time.

statistical analysis of the taken SEM images over 200 polymer particles. Three representative particle sizes where the cumulative curve of the PSD (cf. such as the curves in Figure 3) corresponds to 10, 50 and 90% were plotted for the polymerization time (the zero time values were taken from Figure 3), in comparison with the average particle sizes estimated from the kinetic curve (Figure 1, in the presence of EB). For the Cat-C in Figure 5, all the particle sizes at 10, 50 and 90% grew relatively evenly, although the broadness of the PSD was gradually expanded as the polymerization proceeds. The averaged particle sizes derived from the kinetic curve showed good coincidence with the particle size at 50% for 15 min of the polymerization time in spite of the rough estimate from the kinetic curve, indicating good replication of the catalyst particles at the early stage without significant breakage or aggregation of the polymer (or catalyst) particles. However, as the polymerization time proceeded, the estimated value became smaller than the particle size at 50% (the deviation was *ca.* 23% at 120 min), in consistent with the observed agglomeration in Figure 4. The formation of the agglomerates after the early stage of the polymerization was also observed by McKenna and Mattioli.[17]

Origin of the Kinetic and Morphological Characteristics of the $Mg(OEt)_2$-Based Catalyst

The present results indicated the slow activation-deactivation kinetics for the Cat-C with good replication and uniform growth of all the particles. Finally, we address the origin of the kinetic and morphological characteristics of the Cat-C. As was described already,[9] the basic characters of the active sites are quite similar for different conventional ZN catalysts. However, the different catalyst preparation procedures are expected to cause a large deviation of the spatial distribution of $TiCl_4$ in the catalyst particles. For the Cat-C, spherical $Mg(OEt)_2$ particles are converted to $MgCl_2$[5,18] by the reaction of the ethoxide groups with $TiCl_4$ during catalyst synthesis. Therefore, it is obviously necessary to design a porous or channel structure of original spherical $Mg(OEt)_2$ particles to enable the homogeneous penetration of $TiCl_4$ even inside of the precursor particles and subsequent complete exchange of unnecessary ethoxide groups by $TiCl_4$, suggesting spatially homogeneous placement of $TiCl_4$ in the catalyst particles of Cat-C. It was previously reported with X-ray photoelectron spectroscopy that $MgCl_2$-based catalyst such as ball milled one had Ti distribution concentrated on the particle surface, while that for the chemically activated catalysts such as the Cat-C was uniform over catalyst particles.[19] On the other hand, the Cat-C was believed to show the mild initial activity and long-standing activity because of the uniform Ti distribution all over the catalyst particles,[19,20] which enables continuous exposure of new $TiCl_4$ through the fragmentation for the stable replication and uniform growth of the particles.

Conclusions

The kinetic and morphological behaviors of slurry propylene polymerization with a $Mg(OEt)_2$-based ZN catalyst were investigated in the absence and the presence of 2 typical external donors. The $Mg(OEt)_2$-based catalyst showed slow activation-deactivation kinetics during the polymerization. The external donors including EB and C-donor demonstrated similar trend in the kinetic profiles in comparison with the polymerization in the absence of external donor. However, the EB as an external donor showed the higher activity and stereospecificity than the C-donor. The SEM and PSD results demonstrated good morphology and uniform growth of the polymer particles for the $Mg(OEt)_2$-based catalyst. The origin of the high performance of $Mg(OEt)_2$-based catalyst could be explained by uniform spatial distribution of $TiCl_4$ all over the catalyst particles to successfully control the initial fragmentation process and subsequent stable growth of the polymer particles.

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