Similarities and Differences of the Active Sites in Basic and Advanced MgCl₂-Supported Ziegler-Natta Propylene Polymerization Catalysts

Yuichi Hiraoka, Sang Yull Kim, Ali Dashti, Toshiaki Taniike, Minoru Terano*

Though preparation procedures of heterogeneous Ziegler-Natta catalysts for propylene polymerization are sophisticated, it is uncertain whether the nature of the active sites is similar or different for different preparation procedures. In this study, the effects of preparation procedures on the nature of the active sites were investigated by stopped-flow polymerization in combination with microstructure analysis of polymers. Both basic and advanced types of catalysts showed the same two kinds of isospecific active site, which indicated little influence of the preparation method on the active site structure. On the contrary, the ratios of the two kinds of isospecific sites were not the same, resulting in variation of average polymer properties.

Introduction

Propylene polymerization with heterogeneous Ziegler-Natta (ZN) catalysts today produces more than forty million tons of poly(propylene) (PP) per year worldwide. Since the discovery of MgCl₂ as a catalytic support, the components of the ZN catalysts have been fixed as TiCl₄/internal donor (InD)/MgCl₂ combined with an external donor and alkylaluminum activator, and continuous efforts have been devoted to improving the performance of ZN catalysts. These have focused mainly in two key directions: one is the finding of new donors, since donors directly affect active sites performance—i.e., polymer properties—through stereo and regiospecificity, molecular weight distribution (MWD), etc. The other is the development of synthetic routes to obtain TiCl₄/InD/MgCl₂ solid components, which is important for macroscopic aspects, such as polymerization kinetics, bulk density and morphology of produced PPs, replication and fragmentation behaviors of polymer-catalyst particles, mass and heat diffusion, etc. Of course, these two directions interplay with each other, typically at an intermediate size scale between active sites and catalyst particles. For example, Gupta et al. reported, using X-ray diffraction of catalysts, that the bulk structure and primary particle size of MgCl₂ depended on the kind of internal donor. On the other hand, Noto et al. claimed that the preparation procedure affected the extent of structural disorder of MgCl₂, which was correlated with the catalyst
activity.\(^4\) Moreover, it is known that even with the same internal donor, the obtained polymer properties are not exactly the same for different preparation procedures.\(^5\)

Preparation procedures of MgCl\(_2\)-based ZN catalysts are typically classified into two types: the physical route (Procedure G), employing the grinding of MgCl\(_2\) with InD (Scheme 1); and the chemical route, which is further classified into solution (Procedure S) and chemical reaction procedures (Procedure C). Procedure S utilizes a solution of MgCl\(_2\) in coordinative solvents, such as alcohol, while Procedure C is based on Mg-based precursors (Scheme 1). Recent industrial catalysts have been dominantly synthesized based on Procedures S and C, and a variety of patents differ in the number of times and timing of the addition of InD and TiCl\(_4\), the granulation process of MgCl\(_2\) particles, and so on. The effects of different catalyst preparation procedures on the performance have been mainly investigated in terms of morphology and kinetics. Tait et al.\(^6\) and Dashti et al.\(^7\) studied differences in the particle morphology development and kinetics among different preparation procedures. A ground catalyst with an irregular shape and size showed severe fragmentation at the initial stage of polymerization, while a chemically synthesized spherical catalyst exhibited a rather stable replication of the original catalyst morphology. They reported that the spatial distributions of Ti species in catalyst particles were largely dependent on the preparation procedures. Terano et al. estimated the molar percentage of initially activated Ti species over the whole Ti amount ([C\(^+\)]) by stopped-flow propylene polymerization for differently prepared catalysts, and suggested a similar correlation between the spatial distribution of Ti species and preparation procedures.\(^6\) to those proposed by Tait et al.\(^6\) and Dashti et al.\(^7\) The results of scanning Auger electron microscopy\(^9\) and X-ray photoelectron spectroscopy\(^10\) confirmed that the degrees of localization of Ti species on the particle surface were sensitive to the preparation procedures. Thus, most previous studies have concentrated on the influences of preparation procedures at the particle scale. On the contrary, their effects on the microscopic aspect – i.e., the nature of the active sites – have never been examined, in spite of the clear importance on polymer properties and of the significant evolution of preparation procedures accomplished in the history. Consequently, it would be highly valuable to compare the similarities and differences of the active sites resulting from basic and advanced preparation procedures. In this study, effects of preparation procedures on the nature of the active sites were investigated by kinetic analysis using the stopped-flow polymerization procedure\(^11\) in combination with crystallinity distribution analysis of PPs. It was found that catalyst preparation procedures never affected the nature of each active site, but varied the existing ratio of different types of active site. In other words, the types of polymer fractions included in the whole polymers were the same, but the blend ratio of each fraction with different microstructures was not the same, affecting the whole polymer properties.

### Experimental Part

#### Materials

Propylene of research grade (donated by Japan Polypropylene Co., Ltd.), nitrogen, anhydrous MgCl\(_2\) (specific surface area of 65.1 m\(^2\) g\(^{-1}\)), donated by Toho Titanium Co., Ltd.), anhydrous and spherical Mg(OE\(_2\))\(_2\) (average particle size 28.5 \(\mu\)m), TiCl\(_4\), and triisobutylaluminum (TIBA, donated by Tosoh FineChem Co., Ltd.) were used without further purification. Ethylene (EB) as InD, heptane and toluene were used after dehydration with a 3 Å molecular sieve.

#### Catalyst Preparation

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

**Grinding Procedure (Cat-G)**

Cat-G was prepared as reported previously.\(^1\)\(^2\)\(^3\) Briefly, 36 g of MgCl\(_2\) and 7.8 mL of EB were ground in a 1.2L stainless steel vibration mill pot with 55 balls for 24 h at room temperature. The ground powder was then stirred with 200 mL of TiCl\(_4\) at 90°C in a 1 L three-necked flask for 2 h, followed by washing with heptane.

**Solution Procedure (Cat-S)**

Cat-S was prepared based on the patent of Mitsui PetroChemical Industries, Ltd.\(^1\)\(^4\) After dissolving 10 g of MgCl\(_2\) in 52.5 mL of 2-ethylhexanol and 50 mL of decane at 120°C for 2 h, 5 mL of EB was added to the solution at 120°C. The solution was added dropwise to 400 mL of TiCl\(_4\) at -15°C for 1 h, followed by gradual heating up to...
### Table 1. Composition of the three kinds of catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ti&lt;sup&gt;a&lt;/sup&gt;</th>
<th>EB&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-G</td>
<td>1.83</td>
<td>11.2</td>
</tr>
<tr>
<td>Cat-S</td>
<td>3.97</td>
<td>17.5</td>
</tr>
<tr>
<td>Cat-C</td>
<td>3.28</td>
<td>15.4</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by titration.  
<sup>b</sup>Determined by gas chromatography.

90°C. The obtained solid was washed with heptane, additionally treated with 200 mL of TiCl<sub>4</sub> at 90°C, and washed with heptane.

### Chemical Reaction Procedure (Cat-C)

Cat-C was prepared as described previously. TiCl<sub>4</sub> (80 mL) was added dropwise into 240 mL of toluene slurry containing 40 g of Mg(OEt)<sub>2</sub>, then gradually heated up to 90°C. After the addition of 12 mL of EB, the mixture was kept at 90°C for 2 h. The obtained solid was washed with toluene, additionally treated with 80 mL of TiCl<sub>4</sub> in 200 mL of toluene at 90°C for 2 h, then washed with heptane. The catalyst compositions as prepared by the three kinds of procedures are shown in Table 1. The adsorption states of EB were evaluated by diffuse-reflection infrared Fourier-transform (DRIFT) spectroscopy under an N<sub>2</sub> atmosphere. The carbonyl stretching vibration over 1650 to 1750 cm<sup>-1</sup> was similar among the three preparation methods (Figure 1), which means that the adsorption states of donors were insensitive to the preparation methods.

### Stopped-Flow Polymerization

The stopped-flow polymerization was carried out as reported previously. The catalyst slurry and solution of TiBA in heptane were introduced into separate glass vessels equipped with magnetic stirrers under an N<sub>2</sub> atmosphere. After saturating the two vessels with propylene at 1 atm and 30°C, the catalyst slurry and cocatalyst solution were simultaneously pushed out by N<sub>2</sub> through a Teflon tube with an inner diameter of 2 mm, and were mixed at a T-connector to start the polymerization. The Ti and Al concentrations were respectively set to 2.3 x 10<sup>-4</sup> and 7.0 x 10<sup>-2</sup> mol·L<sup>-1</sup>, corresponding to an Al/Ti ratio of 30. The polymerization time was adjusted from ca. 0.1 to 0.2 s by changing the length of the Teflon tube, and the polymerization slurry was cast into a flask containing ethanol and aqueous HCl to instantaneously terminate the polymerization. The polymer obtained was then washed with distilled water and dried in vacuo, followed by re-precipitation with xylene/a mixture of water and ethanol. The evaluation of kinetic parameters ([C<sup>0</sup>], the molecular ratio of activated Ti species, and k<sub>p</sub>, the propagation rate constant) was conducted with the usual procedure based on the linear fit of the obtained polymerization yield and number-averaged molecular weight in terms of the polymerization time.

### Characterization of PP

The molecular weight and MWD of PP were determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (Tosoh TSK-GEL G3000HHR and G5000HHR) at 140°C using o-dichlorobenzene (ODCB) as a solvent, which contains 0.03 wt.-% of 2,6-di-tert-butyl-p-cresol (BHT) as an antioxidant. H NMR spectra were recorded on a Varian Gemini-300c spectrometer at 120°C with hexafluorobutane-1,3-diene as a diluent and 1,1,2,2-tetrachloroethane-d<sub>2</sub> as the internal lock and reference. The crystallinity distribution of PP was measured by temperature-rising elution fractionation (TREF, Senshu SSC-7300) packed with a Chromosorb column (purchased from Celite Corp.) with ODCB including 0.03 wt.-% of BHT as an extraction solvent. The column loading the sample PP in ODCB was slowly cooled down from 140°C to 20°C over 19 h without eluent flow, and then heated up to 140°C for 10 h to elute the polymer. The eluted solution was analyzed by an IR detector to obtain the crystallinity distribution profile.

### Results and Discussion

Stopped-flow propylene polymerization was conducted using the catalysts in order to investigate the nature of active sites before their transformation by alkylaluminum, and the produced polymer properties. Polymer yields and M<sub>n</sub> increased linearly during the polymerization time for all the catalysts (Figure 2a and b). That is, the amount and nature of the active sites formed initially were constant over the period for all the catalysts, and the obtained polymer was regarded as directly reflecting the nature of the active sites just after formation. Cat-G demonstrated the highest polymer yield, and Cat-C the lowest, having less than half that the yield of Cat-G. This difference in the initial yields is consistent with the ratio of zero-time polymerization yields previously estimated from slurry polymerization. In contrast, Cat-C showed the highest M<sub>n</sub>. The MWDs of the obtained polymers shown in Figure 2c were almost constant for 0.1 to 0.2 s, supporting quasi-living behavior for 0.2 s without chain transfer reactions and an increase of the active site heterogeneity. In addition, the active site heterogeneity was similar among the three catalysts. From the gradients of the initial yield and M<sub>n</sub> with respect to the
polymerization time, values of $k_p$ and [C$^\ast$] of the prepared catalysts were obtained, as summarized in Table 2. The active site concentration, [C$^\ast$], obtained by stopped-flow polymerization for 0.1 to 0.2 s is related to the amount of Ti species, which are initially accessible for the cocatalyst before fragmentation.$^{[18]}$ Such Ti species should reside on the outermost surface of catalyst particles or on the walls of accessible pores inside particles. The fragmentation of catalyst particles, which exposes hidden Ti species, never contributed to [C$^\ast$], since even Cat-G with the highest initial activity gave a polymer yield per gram of catalyst of 0.19 for 0.2 s, which is far from the value associated with fragmentation. Moreover, the fact that the initial polymer yield and $M_n$ had a linear relationship with the polymerization time clearly indicated the instantaneous activation of Ti species and subsequent activation/deactivation never occurred up to 0.2 s. This also rejected the contribution of newly exposed Ti species through fragmentation to [C$^\ast$]. Thus, [C$^\ast$] reflects the amount of Ti species initially placed on the outermost surface or on the walls of accessible pores. For Cat-G with a low porosity, the initially accessible Ti species was considered to mainly exist on the outermost surface. The fact that Cat-G had a much higher [C$^\ast$] than Cat-C suggested that the Ti species are relatively localized on the initially accessible surface for Cat-G, while they are relatively dispersed over the whole particle for Cat-C. This is consistent with previous observations,$^{[6,7]}$ and correlated with a decay-type kinetics for Cat-G and a build-up-type kinetics for Cat-C in normal slurry polymerization. For Cat-S, the results were intermediate between those for Cat-G and Cat-C. Murata et al. claimed that a catalyst particle for Cat-S consisted of aggregated sub-particles of MgCl$_2$, with Ti species being locally concentrated on the surface of each sub-particle.$^{[10]}$ In this manner, our stopped-flow polymerization results give further support for the relationship between the catalyst preparation procedures and the spatial distribution of Ti species over particles. The order of $k_p$ followed the sequence, Cat-C > Cat-S > Cat-G. The same trend was observed for mmmm of the PP.$^6$ These differences in $k_p$ and the stereoregularity of the PP among the preparation procedures implies the presence of a variety of active sites. Consequently, the microstructures of the PP obtained by the stopped-flow polymerization were evaluated by TREF analysis (Figure 3). The elution peaks of PP correspond to the stereoregularity (crystallinity) of the polymer for each fraction.$^{[29]}$ which is generated at an active site with the corresponding isospecificity. The combination of the TREF analysis and the stopped-flow polymerization has been quite powerful for identifying the stereospecificity distribution of active sites in heterogeneous ZN catalysts.$^{[14,27]}$ Because no active site transformation occurs during the initial stage, TREF curves for PP obtained with stopped-flow polymerization generally consists of a relatively small number of sharp elution peaks, reflecting a small number of active sites types, which makes it possible to obtain much more direct information than by normal polymerization. As can be seen in Figure 3, two elution peaks were commonly observed at ca. 105 and 115 °C for all the catalysts, where the lower isotacticity
(equal to the lower isospecificity) at 105 °C is labeled as LI, and the higher as HI. This surprisingly indicated that the same two types of isospecific active sites existed in both of the basic mechanically activated and recent chemically activated catalysts. The detection of the same two elution peaks agreed with the similar MWDs among the differently prepared catalysts, leading to a proposal that the catalyst preparation procedure itself was not relevant to the molecular-level structure of active sites. It should be noted that the active site structure was known to be specific to the kinds of donors. The intensity ratios of the two peaks, namely the ratio between the two kinds of stereospecific sites (HI/LI), were different among the preparation procedures (Figure 3). The higher ratio of the HI site yielded a higher mmm, leading to a larger zp. Specifically, Cat-G had the highest ratio of the LI site with the lowest zp, while Cat-C had the highest ratio of the HI site with the largest zp. From these results, it is clear that the catalyst preparation procedures have an effect on the molecular structure of each active site, but on the proportion of differently isospecific active sites, which differentiate the whole polymer properties by changing the ratio of polymer chains with different primary structures. Additional slurry polymerization was conducted for 10 min with the same conditions as those of the stopped-flow polymerization to confirm the validity of the above conclusion for a longer-time polymerization. The TREF curves of the obtained polymers are shown in Figure 4. Though the two peaks in the TREF curves became broader for the 10 min polymerization, they still possessed the two-peak character, and the centers of the peaks were in the order of Cat-C > Cat-S > Cat-G, consistently with the order of the HI/LI ratio for the 0.2 s polymerization. This suggested that the initial difference of the active sites distribution is basically kept during polymerization.

There are two possible reasons why catalyst preparation procedures affected the existing ratio of active sites. One is the structural difference of MgCl₂ as a support material, and the other is the difference in co-adsorption states between Ti species and InD on MgCl₂. Noto et al. reported that the catalyst preparation procedure affects the microstructure of δ-MgCl₂, so as to differentiate the performance of the resulting catalysts. Moreover, according to a plausible mechanism for the improvement of the isospecificity of active sites based on co-adsorption of InD with Ti species, catalyst preparation procedures might affect the proportion of HI to LI by varying their co-adsorption states.

**Conclusion**

The influences of the catalyst preparation procedure on the nature of active sites were examined by stopped-flow polymerization and TREF analysis. Depending on the kind of procedure, catalysts had largely different initial active site concentrations [C⁺], correlated with the spatial dispersion of Ti species in a catalyst particle. The basic mechanical and advanced chemical procedures gave the same two kinds of isospecific active sites, leading to the important conclusion that catalyst preparation procedures using the same InD hardly affect the molecular structure of active sites. On the other hand, the existing ratio of the two isospecific sites depends on the preparation procedures, which in turn alters the polymer properties, the mechanism of which is very important for the establishment of new catalyst synthetic routes.
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