Deviation of hydrogen response during propylene polymerization with various Ziegler–Natta catalysts

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Abstract

The influence of the catalyst type on the hydrogen response during propylene polymerization with Ziegler–Natta catalysts was investigated in terms of the variations in kinetic behavior, catalyst activity, molecular weight and its distribution, and microstructure of the resulting polymers. Three different types of supported Ziegler catalysts and a $TiCl_3$ catalyst were used in this study. In all cases, the catalyst activity was found to significantly increase with the addition of hydrogen along with a sharp decrease in the molecular weights. The activity enhancement by hydrogen was remarkable during polymerizations with supported catalysts compared to the case of a $TiCl_3$ catalyst system. Hydrogen was found to activate all of the supported catalysts to same degree, regardless of the type of internal donor and the preparation method. This phenomenon is considered to be mainly ascribed to no significant difference in the number of dormant sites formed on the supported catalysts. The influence of the catalyst type on the hydrogen response was remarkable for the molecular weight and its distributions, which may be due to the difference in the states of the active species on each catalyst. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Hydrogen has been used as a chain-transfer agent to control the molecular weight of the polymer for the commercial production of poly-olefins such as polypropylene and polyethylene. After the discovery of the efficiency of hydrogen as a modifier, much effort has been devoted by many research groups to elucidate the action of the hydrogen for many Ziegler–Natta catalyst systems. However, the effect of hydrogen, particularly the mechanisms of the activation behavior and the chain-transfer reaction, remains one of the obscure aspects in the field of olefin polymerization with Ziegler–Natta catalysts. One of the main reasons for this uncertainy is that the active sites on the heterogeneous catalysts are extremely complex, and the catalyst performance including the hydrogen response is drastically affected by the preparation method of the catalyst as well as the kind of material used in the catalyst.

The effect of hydrogen on the rate of olefin polymerization with Ziegler–Natta catalysts is

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rather complex [1,2]. Depending on the types of catalyst, co-catalyst, monomer, and polymerization conditions, the polymerization rate can either decrease, increase, or remain unaffected in the presence of hydrogen. As for the propylene polymerization with a heterogeneous supported Ziegler catalyst, the activity enhancement effect was published by Guastalla and Giannini [3], who observed a significant increase in polymerization rate upon adding hydrogen to the catalyst system comprised of $TiCl_4/MgCl_2$ and triethylaluminium (TEA). Soga and Shiono [4], however, demonstrated that the addition of hydrogen during propylene polymerization with $TiCl_4$/ethylbenzoate (EB), $AlCl_3/MgCl_2$–TEA/EB caused a decrease in the catalyst activity and stereospecificity. The activity in propylene polymerization of the catalyst based on $TiCl_4/EB/MgCl_2$–TEA/2,2,6,6-tetramethylpiperidine was reported to be lowered by hydrogen [5]. Several authors have reported the hydrogen activation effect observed when using $TiCl_4/EB/MgCl_2$ [6,7], $TiCl_4$/phthalate ester/$MgCl_2$ [8–13], $TiCl_4$/diether/$MgCl_2$ [14,15] in combination with TEA and an external donor. Chadwick et al. [11] remarked that the magnitude of the hydrogen activation effect observed with the $TiCl_4$/phthalate ester/$MgCl_2$ catalyst was affected by the kind of alkoxysilane used as the external donor in the polymerization. The hydrogen activation effect has also been reported for homogeneous catalyst systems [16–19]. As far as the propylene polymerization with the $TiCl_3$-based catalyst system, the polymerization rate with $TiCl_3$–TEA has been found to be substantially reduced by hydrogen [20]. Whereas, the opposite tendency was observed in the case of the polymerization with AA-$TiCl_3$ (δ-$TiCl_3 \cdot 0.33$ $AlCl_3$) and diethylaluminium chloride (DEAC) [21,22]. Although the effect of hydrogen during olefin polymerization has been an object of study for a long time, there is little agreement as to hydrogen response, that is the degree of the changes in the activity, molecular weight, and other factors by the addition of hydrogen as well as

theories on how hydrogen may effect on these factors. In particular, the correlation of the catalyst type to the hydrogen effect has not been clarified yet, even though the difference in the hydrogen response between the monoester-type and diester-type supported Ziegler catalysts is commonly known in the industrial field.

In this study, a comparison of the hydrogen response to propylene polymerization with various types of Ziegler–Natta catalysts is made in terms of the variations in kinetic behavior, the catalyst activity, molecular weight and its distribution, and microtacticity. The main emphasis falls on the dependence on the hydrogen response of catalyst systems involving the kinds of internal donor and magnesium compound used in the catalyst, and the catalyst preparation method. The estimation of the catalyst type-induced difference in the hydrogen response is considered to provide profound insights into not only the action of hydrogen during olefin polymerization but also the interaction of hydrogen with the active sites on the various types of catalysts.

2. Experimental

2.1. Materials

Propylene (donated by Chisso and Mitsubishi Chemical) and H_2 (purchased from Nippon Sanso, 99.9999%) were used without further purification. Heptane and toluene (Wako) were used after dehydration by passing through a molecular sieve 13-X column. EB (Wako) and dibutylphthalate (DBP, Wako) were used as internal donors after dehydration with molecular sieves. Anhydrous $MgCl_2$, $Mg(OEt)_2$ (donated by Toho Titanium), $TiCl_4$ (Wako), and pure nitrogen (Uno Sanso) were used without further purification. TEA and DEAC were kindly donated by Tosoh Akzo and used as heptane solutions.

2.2. Catalysts preparations

Three different types of supported Ziegler catalysts and a $TiCl_3$ catalyst were used to clarify the effect of the catalyst type on the hydrogen response during propylene polymerization. The preparation procedure and Ti content of each catalyst are summarized in Table 1. AA-$TiCl_3$ (δ-$TiCl_3 \cdot 0.33$ $AlCl_3$, Cat-D) was donated by the Toho Titanium.

Cat-A, in which EB was cited as the internal donor, was prepared by means of co-grinding $MgCl_2$ and EB followed by the reaction with $TiCl_4$ [23]. The $MgCl_2$ (30 g; 11 m^2 g^{-1}) and ethyl benzoate (6.5 ml) were placed in a 1-l stainless steel vibration mill pot with 50 balls (25 mm diameter) under nitrogen and ground for 30 h at room temperature. The ground powder (6.1 g) was allowed to react with $TiCl_4$ (200 ml) in a 500-ml three-necked flask at 90°C for 2 h with stirring under nitrogen, followed by sufficient washing with heptane.

Cat-B was prepared by co-grinding $MgCl_2$ and DBP followed by the reaction with $TiCl_4$ using the similar procedures of Cat-A, except for the use of DBP as the internal donor instead of EB.

Cat-C was prepared by reacting $TiCl_4$ with the mixture of $Mg(OEt)_2$ and DBP as follows: $Mg(OEt)_2$ (10 g) and $TiCl_4$ (20 ml) in toluene (80 ml) were heated to 90°C, and mixed with DBP (2.7 ml) at 115°C for 2 h. The mixture was washed with toluene, then the residue was reacted again with $TiCl_4$ (20 ml) and toluene (80 ml) at 115°C for 2 h. Finally, the obtained catalyst was washed several times with heptane.

2.3. Slurry polymerization of propylene

The slurry polymerization of propylene (1 kgf cm^{-2}) was typically performed with the supported Ziegler catalyst (0.040 mmol Ti) and TEA ([Al] = 20 mmol l^{-1}, Al/Ti molar ratio = 100) in heptane (200 ml) at 60°C for 30 min. The polymerization was also carried out with AA-$TiCl_3$ (4.0 mmol Ti) and DEAC ([Al] = 100 mmol l^{-1}, Al/Ti molar ratio = 5.0). The time when the desired amount of co-catalyst was added to the propylene-saturated heptane containing the catalyst was defined as the starting time of the polymerization. The monomer concentration in the polymerization system was maintained by the flow of monomer through a flow meter (Laminar Flow Meter: Model 536, Metabo; Micro-Pressure Transducer: DP45, Validyne) according to the consumption by the polymerization. Therefore, the polymerization rate was monitored as the amount of monomer consumption by means of the monomer flow meter. Hydrogen was added as appropriate by syringe into the headspace above the slurry. After the polymerization, the reaction system was quenched with ethanol containing 20 vol.%

Table 1
Characterization of Ziegler–Natta catalysts used in this study

Catalyst (components)	Preparation method	Titanium content[a] (mmol Ti g cat.$^{-1}$)
Cat-A ($TiCl_4$/EB[b]/$MgCl_2$)	co-grinding $MgCl_2$ and EB, followed by the reaction with $TiCl_4$	0.40
Cat-B ($TiCl_4$/DBP[c]/$MgCl_2$)	co-grinding $MgCl_2$ and DBP, followed by the reaction with $TiCl_4$	0.36
Cat-C ($TiCl_4$/DBP[c]/$Mg(OEt)_2$)	reacting $TiCl_4$ with the mixture of $Mg(OEt)_2$ and DBP	0.61
Cat-D (δ-$TiCl_3$/0.33 $AlCl_3$)	AA-type $TiCl_3$, donated from Toho Titanium	(24.1 mol%)

[a]Measured by titration method.
[b]EB: ethylbenzoate.
[c]DBP: dibutylphthalate.

of conc. HCl: then the obtained polymer was washed with a large amount of distilled water and dried in vacuo.

The polymerization of propylene (8 kgf cm^{-2}) was also performed in a 1-l glass autoclave reactor (TEM-V1000N, Taiatsu Techno) with the supported Ziegler catalyst (Cat-A and Cat-B = 0.0033 mmol Ti, Cat-C = 0.0017 mmol Ti) and TEA (Al/Ti molar ratio = 300) in heptane (500 ml) at 70°C for 60 min. The polymerization was also carried out with AA-TiCl$_3$ (0.50 mmol Ti) and DEAC ([Al] = 5.2 mmol l^{-1}, Al/Ti molar ratio = 5.2) in heptane (500 ml) at 70°C for 60 min. The polymerization rate was monitored as the flow of monomer by using a mass flow meter (Model 3920, Kofloc).

2.4. Measurements

The molecular weight and its distribution of the obtained polymer were determined by gel permeation chromatography (GPC, Senshu SSC-7100) with a polystyrene gel column (Jordi-Gel DVB Mixed Bed) at 140°C using o-dichlorobenzene as the solvent. The ^{13}C NMR spectra were recorded on a Varian Gemini-300 spectrometer at 120°C in 20% (w/v) solution of 1,2,4-trichlorobenzene. Ten percent (v/v) benzene-d_6 was added as an internal lock, and hexamethyldisiloxane was used as an internal chemical shift reference.

3. Results and discussion

3.1. Insights into the catalyst constituent and preparation method

Ziegler–Natta catalysts are typically conjugates formed by the interaction of groups I–III metal compounds involving alkylaluminiums (the co-catalyst) with transition metal compounds such as TiCl$_3$ or TiCl$_4$ (the catalyst). Some other compounds, such as electron donors, are often employed as a third component of the catalyst system. Each component and the cata-

lyst preparation method have a significant effect on the catalyst performance as well as the nature of the active sites on the catalysts. As mentioned in the Introduction, our attention was focused on the correlation of the hydrogen response to the catalyst system involving the kinds of internal donor and magnesium compound used in the catalyst, and the catalyst preparation method. A good understanding the relationship between the nature of the active sites, catalyst performance including the hydrogen response, and the catalyst preparation method is of great importance to obtain a deeper insights of the basic aspects, which will lead to further development of the area.

Among the various preparation methods of highly active Ziegler catalysts, the ball-milling method has been widely employed to overcome the low surface area which induces the poor interaction of MgCl$_2$ and TiCl$_4$ [24]. The practical effect of ball-milling is to break the crystal structure and to increase the surface area of MgCl$_2$. One of the most effective ways of preparing such catalysts takes place in two steps [25]: (i) milling of anhydrous MgCl$_2$ with an electron donor compound; and (ii) treatment of the product of the first step (i) with TiCl$_4$. The internal electron donor, such as a monoester, diester, or diether compounds, is used as an important third component during the catalyst preparation procedure, which is almost indispensable to obtain the polypropylene having satisfactory stereoregularity. Therefore, two types of supported Ziegler catalysts containing different internal donors (EB and DBP) were employed as samples in order to clarify the influence of the kind of internal donor on the hydrogen response. The supported Ziegler catalysts were prepared by grinding MgCl$_2$ with EB followed by the reaction with TiCl$_4$ (Cat-A), and by grinding MgCl$_2$ with DBP followed by the reaction with TiCl$_4$ (Cat-B). Another practical approach to obtain supported Ziegler catalysts is the preparation from the reaction between Mg(OR)$_2$ and TiCl$_4$ in the presence of an electron donor, which shows a very high activ-
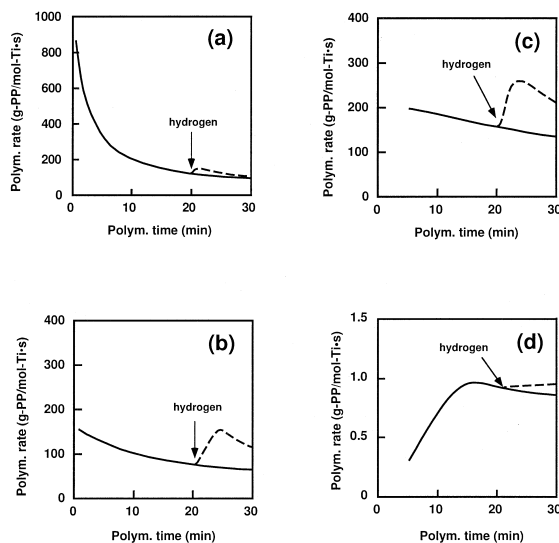
Fig. 1. Relation of time with the rate for slurry polymerization of propylene (1 kgf cm^{-2}): (a) Cat-A; (b) Cat-B; (c) Cat-C; (d) Cat-D. The solid line indicates the results without hydrogen. The dotted line indicates the results when hydrogen (5 ml) was introduced to the system during the polymerization.

ity and selectivity for the propylene polymerization [26]. On the basis of the consideration, another type of supported catalyst (Cat-C) was prepared by reacting $TiCl_4$ with the mixture of $Mg(OEt)_2$ and DBP. The third catalyst is one example of the modern industrial catalysts used in current commercial processes for polypropylene production. The detailed preparation condi-

tions were adjusted to give the supported Ziegler catalysts having a certain amount of titanium content (ca. 0.35–0.65 mmol Ti g cat.$^{-1}$), as shown in Table 1 and Section 2. AA-TiCl$_3$ (Cat-D) was also cited as an example of non-supported catalysts.

3.2. Study of hydrogen response on propylene polymerization with various Ziegler–Natta catalysts

The hydrogen response during olefin polymerization with these important classes of Ziegler–Natta catalysts obtained by the different preparation methods was investigated in terms of the variation in polymerization behavior. In all cases, the propylene polymerization was carried out without an external donor to avoid the unfavorable interaction of the internal and external donors, and to clearly evaluate the influence of the catalyst type on the hydrogen response. The slurry polymerization of propylene (1 kgf cm^{-2}) was conducted using three types of supported Ziegler catalysts with TEA at 60°C for 30 min in the presence and absence of hydrogen, and the polymerization rate was measured by evaluating the monomer consumption. The AA-TiCl$_3$/DEAC catalyzed polymerization was also performed. The solid lines in Fig. 1(a)–(d)

Table 2
Slurry polymerization of propylene (1 kgf cm^{-2}) with various Ziegler–Natta catalysts[a]

Run	Catalyst system	Hydrogen	Activity (kg PP mol Ti^{-1})	$\overline{M}n$[b]	$\overline{M}w/\overline{M}n$[b]	$mmmm$[c] (%)
1	Cat-A/TEA[d]	absent	223	5200	5.1	68.1
2	Cat-A/TEA[d]	present[f]	276	4700	6.1	68.2
3	Cat-B/TEA[d]	absent	170	10 000	5.1	73.5
4	Cat-B/TEA[d]	present[f]	210	7000	7.0	75.1
5	Cat-C/TEA[d]	absent	245	26 000	4.1	76.6
6	Cat-C/TEA[d]	present[f]	306	25 000	3.7	77.7
7	Cat-D/DEAC[e]	absent	1.11	74 000	7.7	94.5
8	Cat-D/DEAC[e]	present[f]	1.35	71 000	7.8	95.9

[a] Propylene polymerization was carried out in heptane (200 ml) at 60°C for 30 min.
[b] Determined by GPC.
[c] Determined by ^{13}C NMR.
[d] Triethylaluminium ([Al] = 20 mmol l^{-1}, Al/Ti molar ratio = 100).
[e] Diethylaluminium chloride ([Al] = 100 mmol l^{-1}, Al/Ti molar ratio = 5.0).
[f] Hydrogen (5 ml) was introduced after the polymerization for 20 min.

Table 3
Slurry polymerization of propylene (8 kgf cm^{-2}) with various Ziegler–Natta catalysts[a]

Run	Catalyst system	Hydrogen	Activity (kg PP mol Ti^{-1})	$\overline{M}n$[b]	$\overline{M}w/\overline{M}n$[b]	*mmmm*[c] (%)
9	Cat-A/TEA[d]	absent	8000	40 000	8.8	57.7
10	Cat-A/TEA[d]	present[f]	12 200	25 000	5.2	64.3
11	Cat-B/TEA[d]	absent	2540	43 000	7.1	63.7
12	Cat-B/TEA[d]	present[f]	4000	21 000	5.8	66.2
13	Cat-C/TEA[d]	absent	8100	73 000	6.4	68.9
14	Cat-C/TEA[d]	present[f]	12 700	28 000	7.6	70.8
15	Cat-D/DEAC[e]	absent	60	–	–	–
16	Cat-D/DEAC[e]	present[f]	77	–	–	–

[a] Propylene polymerization was carried out in heptane (500 ml) at 70°C for 60 min.
[b] Determined by GPC.
[c] Determined by ^{13}C NMR.
[d] Triethylaluminium (Al/Ti molar ratio = 300).
[e] Diethylaluminium chloride (Al/Ti molar ratio = 5.2).
[f] Polymerization was performed in the presence of hydrogen (100 ml).

show the polymerization curves without hydrogen. The initial activity of the polymerization with the Cat-A/TEA system was very high followed by a drastic decay. It may be that the titanium species on Cat-A are activated at the beginning of the polymerization, followed by a progressive reduction in the titanium species that reduces the number or efficiency of the active sites with time. The polymerization using the supported catalysts containing DBP as an internal donor (Cat-B and Cat-C) showed a lower decay rate compared with the catalyst containing EB (Cat-A). This phenomenon is thought to be mainly governed by the difference in the feasibility of the replacement and/or desorption of the internal donor by TEA, depending upon the kind of internal donor used in the catalysts. The rate-time profile for the polymerization with TiCl$_3$ (Cat-D)/DEAC was apparently different from that with the supported Ziegler catalysts. The introduction of a small amount of hydrogen (5 ml) to the polymerization system caused a rapid increase in the polymerization rate, as can be seen by the dotted lines in Fig. 1. Table 2 shows the results of the propylene polymerization (1 kgf cm^{-2}) with and without hydrogen. The slight decrease in the molecular weight associated with the activ-

ity enhancement was observed by the introduction of hydrogen, regardless of the catalyst systems. The introduction of hydrogen was also found to induce a slight increase in the meso pentad fraction (*mmmm*, %) of the obtained polypropylenes. However, there was no specific tendency in the variations of the molecular weight distributions.
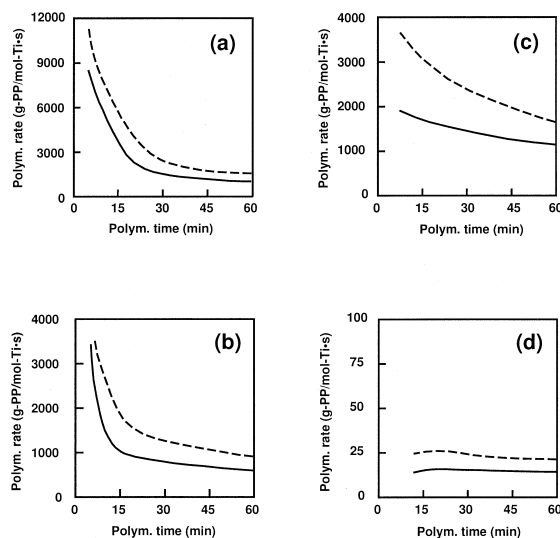

Fig. 2. Relation of time with the rate for slurry polymerization of propylene (8 kgf cm^{-2}): (a) Cat-A; (b) Cat-B; (c) Cat-C; (d) Cat-D. The solid line indicates the results without hydrogen. The dotted line indicates the results with hydrogen (100 ml).

Table 4
Results of decay rate during propylene polymerization (8 kgf cm^{-2}) with various Ziegler–Natta catalysts[a]

Catalyst system	Average decay rate[b] (g PP mol Ti^{-1} s^{-2})	
	Without hydrogen	With hydrogen
Cat-A/TEA	1.7	2.1
Cat-B/TEA	0.29	0.58
Cat-C/TEA	0.28	0.38
Cat-D/DEAC	0.0011	0.0020

[a]The original data are taken from Fig. 2.
[b]The average decay rate was estimated from the slope in the period from 10 to 60 min.

For obtaining more precise information concerning the effect of the catalyst type on the hydrogen response, the polymerization of propylene (8 kgf cm^{-2}) was also performed in a 1-l glass autoclave reactor in the presence and absence of hydrogen. As shown in Table 3, the catalyst activity significantly increased by the addition of hydrogen, together with the sharp decrease in the molecular weights. This indicates that hydrogen has a significant influence on both the chain transfer reaction and the activity enhancement, regardless of the type of catalysts. The values of the meso pentad fraction (*mmmm*, %) of polypropylenes obtained with hydrogen were slightly higher than those obtained without hydrogen. The influence of hydrogen on the molecular weight distribution showed no such propensity. A comparison of the solid and dotted lines in Fig. 2 indicates that

the use of hydrogen leads to an increase in the initial polymerization rate without a significant difference in the rate-time profile for polymerization with each catalyst. The final productivity of catalyst system is typically governed by the combination of the initial polymerization rate and decay rate during the polymerization. In order to obtain more detailed information concerning the rate decay, the slopes of the decay curves during the polymerization (10–60 min) were estimated, the results of which are shown in Table 4. In all cases, the values of the average decay rates with hydrogen were apparently higher than those without hydrogen, suggesting that the number or efficiency of the activated titanium species may be affected by hydrogen during the polymerization. These results indicate that productivity enhancement by hydrogen is mainly due to the increase in the initial polymerization rate, whereas hydrogen exerts no or a slight negative influence on the decay rates under the conditions used in this study.

3.3. Comparison of hydrogen response and discussion

Table 5 lists the gaps in the values of activity, molecular weight, and its distribution, and the microstructure obtained with and without

Table 5
Gaps in values of activity, molecular weight and its distribution, and microstructure obtained with and without hydrogen[a]

Propylene pressure (kgf cm^{-2})	Catalyst system	Δ activity (kg PP mol Ti^{-1})	$\Delta \overline{M}n$	$\Delta \overline{M}w / \overline{M}n$	Δ*mmmm* (%)
1.0	Cat-A/TEA	+53	−500	+1.0	+0.1
	Cat-B/TEA	+40	−3000	+1.9	+1.6
	Cat-C/TEA	+61	−1000	−0.4	+1.1
	Cat-D/DEAC	+0.24	−3000	+0.1	+1.4
8.0	Cat-A/TEA	+4200	−15000	−3.6	+6.6
	Cat-B/TEA	+1640	−22000	−1.3	+2.5
	Cat-C/TEA	+4600	−45000	+1.2	+1.9
	Cat-D/DEAC	+17	–	–	–

[a]The comparison is based on the results for the propylene polymerization (original data are taken from Tables 2 and 3. The Δ values were derived by subtracting the activity, $\overline{M}n$, $\overline{M}w/\overline{M}n$, and *mmmm* obtained without hydrogen from those with hydrogen.

hydrogen. The ratios of the activities, as well as the molecular weights are also shown in Table 6, which correspond to the degree of the changes in these values by the addition of hydrogen. The activity enhancement by hydrogen was remarkable during polymerizations with supported catalysts compared to the case of the $TiCl_3$ catalyst system. For the polymerization with the supported catalysts, the ratios of the activities with hydrogen to those without hydrogen are almost the same (1.23–1.25 and 1.53–1.57 for the polymerizations at 1 and 8 kgf cm^{-2}, respectively). This indicates that hydrogen activates all of the supported catalysts to the same degree, regardless of the internal donor type and the preparation method. Concerning the influence of hydrogen on the molecular weight, many authors have described that the molecular weight decrease by the chain transfer reaction depends on the square root of the partial pressure of hydrogen in heterogeneous catalyst systems [1,27–29]. However, the apparent difference in the molecular weight decrease was observed between Cat-B and Cat-C, even if the DBP was used as an internal donor in the both catalysts. The degree of the change in molecular weight obtained with the catalyst containing EB (Cat-A) was found to be lower than those of the catalysts having DBP (Cat-B and Cat-C) in the polymerization under a higher pressure (8 kgf cm^{-2}). Based on the results obtained in this study, therefore, it seems reasonable to postulate that the deviation in the degree of the molecular weight decrease is present and depends upon the type of catalysts. This is a valid assumption that

the action of hydrogen as a modifier for controlling the molecular weight of the resulting polypropylene is affected not only by the hydrogen pressure but also by the type of catalysts. This is a fact little understood in the past but it is a very essential one.

The catalyst type-induced difference in the hydrogen response has been clarified by the present study. The influence of the catalyst type on the hydrogen response was remarkable for the molecular weight and its distributions, whereas the difference in the degree of the activity enhancement between the supported Ziegler catalysts was negligibly small. It may now be worthwhile by considering this fascinating subject more closely. Recently, several authors suggested that the activating effect of hydrogen can be ascribed to regeneration of the active sites following chain transfer with hydrogen at the dormant 2,1-inserted sites [10–16] or the allylic dormant structure [30,31]. In a preceding article [32], we reported the kinetic investigation of the activity enhancement effect of hydrogen with $TiCl_4 / EB / MgCl_2$ using stopped-flow and conventional slurry polymerization techniques, indicating that the reactivation of the dormant sites by hydrogen is a feasible reason for the activity enhancement. Concerning the action of hydrogen as a chain transfer agent, it was apparent that the chain transfer reaction took place through atomic hydrogen formed by the dissociation of the hydrogen molecule on the modified active species, where the reduction of titanium species was believed to occur and yield lower oxidation

Table 6
Ratios of activity and molecular weight obtained by the polymerization with hydrogen to those without hydrogen[a]

Catalyst system	Activity$_H$/activity$_0$		$\overline{Mn}_H / \overline{Mn}_0$	
	1.0 kgf cm^{-2}	8.0 kgf cm^{-2}	1.0 kgf cm^{-2}	8.0 kgf cm^{-2}
Cat-A/TEA	1.24	1.53	0.90	0.63
Cat-B/TEA	1.24	1.57	0.70	0.49
Cat-C/TEA	1.25	1.57	0.96	0.38
Cat-D/DEAC	1.22	1.28	0.96	–

[a]The comparison is based on the results for the propylene polymerization (original data are taken from Tables 2 and 3: activity$_H$, $\overline{Mn}_H$ indicate the results with hydrogen, while activity$_0$, $\overline{Mn}_0$ indicate the results without hydrogen.

states by reaction with a co-catalyst [23,33]. The results obtained in the present study demonstrated that the degree of the activity enhancement by hydrogen was almost the same, irrespective of the type of supported Ziegler catalysts. On the basis of this consideration combined with our series of studies, it is assumed that there are no significant differences in the number of dormant sites formed during the polymerization with the supported Ziegler catalysts, but the states of the titanium species are different for each catalyst, resulting in the deviation of hydrogen response to the molecular weight and its distribution of the resulting polypropylenes. Needless to say, the subject concerning the hydrogen response is rather complex and seems to involve unknown factors, such as the kind of external donor used during the polymerization and the polymerization process employed in both the laboratory and industry. Further investigations will lead to a comprehensive understanding of these subjects.

4. Conclusion

A comparison of the hydrogen response during propylene polymerization with various types of Ziegler–Natta catalysts has been made as a study of the effect of hydrogen on the activity enhancement and chain transfer reaction. In all cases, the catalyst activity was found to significantly increase by the addition of hydrogen, together with a remarkable decrease in the molecular weights. The activity enhancement by hydrogen was more significant in polymerizations with supported Ziegler catalysts compared with the case of the TiCl$_3$ catalyst system. The difference in the degree of the activity enhancement by hydrogen between the supported Ziegler catalysts was negligibly small. As for the polymerization with the supported Ziegler catalysts, the catalyst type-induced difference in the hydrogen response was significant for the molecular weight and its distributions. These phenomena are considered to be due to the fact that the

activity enhancement mainly depends on the number of dormant sites formed, whereas the chain-transfer reaction is related closely to the states of the titanium species on each catalyst during the polymerization This finding has a great significant from a scientific aspect for olefin polymerization with Ziegler–Natta catalysts and the industrial viewpoint, such as exploiting state-of-the-art catalysts.

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