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STUDY OF THE ACTIVITY ENHANCEMENT CAUSED BY THE ADDITION OF HYDROGEN IN OLEFIN POLYMERIZATION

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ABSTRACT

Propene and 1-butene polymerizations were performed using the catalyst system of $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{diethylphthalate (DEP)/AlEt}_3/\text{phenyltriethoxysilane (PES)}$. In both polymerizations, the activities were enhanced more than three times by the hydrogen addition, while in the catalyst system not containing DEP and/or PES, the degree of the activity enhancement was decreased to about one-third of that in the above catalyst system. The results of a kinetic study on 1-butene short-term polymerization suggest that the said enhancement is not due to the increase of the number of active sites.

INTRODUCTION

It is well known that the catalyst system of $\text{Mg} \cdot \text{Ti} \cdot \text{organic diester organo aluminum/Si-O-C}$ group containing silane compound shows an extremely high activity and high stereospecificity [1–3]. We reported that the activity in this catalyst system was enhanced by the addition of hydrogen to the polymerization system [4]. In order to clarify the reasons for this enhancement, a study was carried out using the catalyst system

of $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{diethylphtharate}$ (DEP)/ AlEt_3 /phenyltriethoxysilane (PES).

EXPERIMENTAL

Preparation of Catalyst

$\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DEP}$ Catalyst

Twenty grams of MgCl_2 was comilled with 6.0 mL of DEP and 3.3 mL of TiCl_4 in an 800-mL stainless-steel pot containing 2.8 kg of stainless-steel balls (15 mm diameter) for 12 h under nitrogen. The comilled product was suspended with 200 mL of 1,2-dichloroethane for 2 h at 80°C. The solid product was filtrated and washed with *n*-decane. The said product ($\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DEP}$ catalyst) contained 2.3 wt% of Ti atoms.

$\text{MgCl}_2 \cdot \text{TiCl}_4$ Catalyst

The preparation procedure of $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DEP}$ catalyst was repeated except for the addition of 6.0 mL of DEP. $\text{MgCl}_2 \cdot \text{TiCl}_4$ catalyst contained 3.0 wt% of Ti atoms.

Polymerization

Five hundred milliliters of *n*-decane were put into 1-L glass flask equipped with a stirrer, followed by introduction of propene or 1-butene with or without hydrogen. AlEt_3 -, PES-, and MgCl_2 -supported Ti catalyst were added and polymerization was performed for a predetermined time at 60°C under atmospheric pressure. After completion of polymerization, 10 mL of 2-methyl-1-propanol was added to the system to stop the polymerization and the reaction mixture was poured into the mixture of 2 L of methanol and 2 L of acetone containing a small amount of HCl. The resulting solid polymer was collected and dried under reduced pressure.

Characterization of Polymer

The average molecular weights and molecular weight distributions of polymers were measured by GPC (Water Associates, Model ALC/GPC 150C), using a mixed polystyrene gel column (10^6 – 10^3 Å pore size) and *o*-dichlorobenzene as solvent at 135°C.

Fractionation of Polymer

Three grams of the polymer sample was dissolved in 500 mL of *n*-decane at 130°C, cooled to 23°C. The resulting precipitated polymer was separated by the filtration and the amount of polymer dissolved in the filtrate (23°C *n*-decane soluble fraction) was measured. The isotactic index (II) was determined by extraction with boiling heptane for 6 h.

RESULTS AND DISCUSSION

The influence of hydrogen addition was investigated in propene polymerization using $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DEP}/\text{AlEt}_3/\text{PES}$ catalyst system (Table 1). With the increase of hydrogen concentration from 0 to 2 mol% in fed propene gas, the molecular weight of polymer was decreased from 3.0 to 1.6 dL/g by intrinsic viscosity and the activity was increased from 290 to 950 g-PP/mmol-Ti·hr·atom. The II of the polymer was unchanged, indicating that the activity was enhanced for both isospecific site and aspecific site. Next, we investigated the influence of hydrogen addition in the catalyst system containing neither DEP nor PES, nor both ($\text{MgCl}_2 \cdot \text{TiCl}_4/\text{AlEt}_3/\text{PES}$, $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DEP}/\text{AlEt}_3$, $\text{MgCl}_2 \cdot \text{TiCl}_4/\text{AlEt}_3$). The observed degree of activity enhancement in these catalyst systems was around 50% of $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DEP}/\text{AlEt}_3/\text{PES}$ system

TABLE 1. Effect of Hydrogen Amount Added in Propene Polymerization

H ₂ conc. (mol%)	Yield (g)	b.p. - C ₇ extraction			23°C - C ₁₀ soluble			(η) (dL/g)
		Insol (wt%)	Sol (g)	Insol (g)	Sol (wt%)	Sol (g)	Insol (g)	
0	14.5	96.0	0.6	13.9	3.20	0.46	14.0	3.03
0.5	31.9	96.2	1.2	30.7	2.62	0.84	31.1	2.12
1.0	37.7	95.9	1.5	36.2	2.48	0.93	36.8	1.89
2.0	47.5	95.5	2.1	45.4	2.83	1.34	46.1	1.59
6.6	41.7	95.4	1.9	39.8	1.95	0.81	40.9	1.37

Polymerization condition: 60°C, 1 h under atmospheric pressure, 0.1 mmol·L⁻¹ of Ti, 0.6 mmol·L⁻¹ of PES, and 6.0 mmol·L⁻¹ of AlEt₃ in 0.5 L of *n*-decane, 60 L·h⁻¹ of propene feed rate.

TABLE 2. Effect of Hydrogen Addition on the Activity in Propene Polymerization

Catalyst system	H ₂ conc. (mol%)	b. p. - C ₇ extraction				23°C - C ₁₀ Soluble			
		Yield (g)	Insol (wt%)	Sol (g)	Insol (g)	Sol (wt%)	Sol (g)	Insol (g)	η (dL/g)
MgCl ₂ ·TiCl ₄ ·DEP/PES/AIEt ₃	0	14.5	96.0	0.6	13.9	3.2	0.5	14.0	3.03
	2.0	47.5	95.5	2.1	45.4	2.8	1.3	46.1	1.59
MgCl ₂ ·TiCl ₄ ·DEP/AIEt ₃	0	21.9	74.6	5.6	16.3	13.8	3.2	18.9	1.78
	2.0	36.3	81.8	6.9	29.7	10.3	8.4	28.2	1.14
MgCl ₂ ·TiCl ₄ /AIEt ₃	0	31.7	23.9	24.1	7.6	51.6	16.4	15.3	1.06
	2.0	40.0	21.6	31.4	8.6	57.5	23.0	17.0	0.51
MgCl ₂ ·TiCl ₄ /PES/AIEt ₃	0	16.6	70.3	4.9	11.7	21.5	3.6	13.0	2.55
	2.0	25.0	73.2	6.7	18.3	17.6	4.4	20.6	1.13

Polymerization conditions: 60°C, 1 h under atmospheric pressure, 0.1 mmol·L⁻¹ of Ti, (2.0 mmol·L⁻¹ of PES), and 6 mmol·L⁻¹ of AIEt₃ in 0.5 L of *n*-decane, 60 L·h⁻¹ of propene feed rate.

TABLE 3. Results of 1-Butene Polymerization

H ₂ conc. (mol%)	Yield (g)	23°C - C ₁₀ insoluble			(η) (dL/g)
		Insol (wt%)	Insol (g)	Sol (g)	
0	8.5	95.7	8.1	0.4	2.62
2.0	73.3	97.5	71.5	1.8	1.23

Catalyst: MgCl₂·TiCl₄·DEP/PES/AlEt₃. Polymerization conditions: 60°C, 1 h under atmospheric pressure, 0.1 mmol·L⁻¹ of Ti, 2.0 mmol·L⁻¹ of PES, and 6.0 mmol·L⁻¹ of AlEt₃ in 0.5 L of *n*-decane, 60 L·h⁻¹ of 1-butene feed rate.

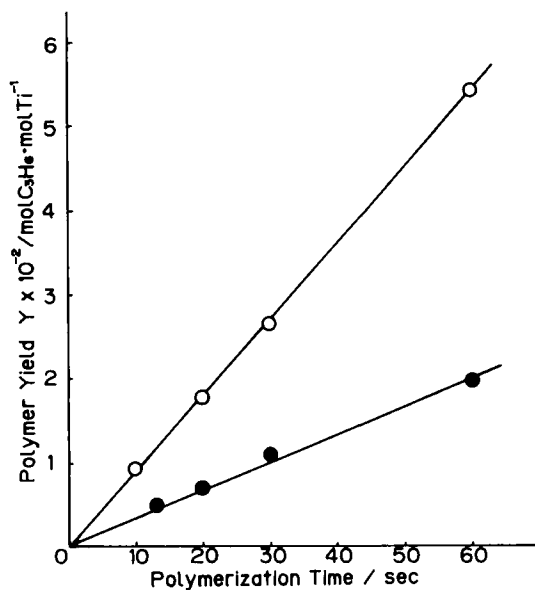


FIG. 1. Time dependence of the polymer yield. ●, Hydrogen absence; ○, hydrogen presence.

TABLE 4. Results of 1-Butene Short-term Polymerization

Time (s)	H ₂ conc. (mol%)	Polymer yield				
		g	mol·molTi ⁻¹	Mw/Mn	Mn × 10 ⁻⁴	n × 10 ²
13	0	0.127	45.4	6.81	2.60	9.8
20	0	0.190	67.9	7.89	2.98	12.8
30	0	0.305	109	7.94	3.00	20.3
60	0	0.545	195	8.67	3.31	33.0
10	2.0	0.257	91.8	6.31	2.55	20.2
20	2.0	0.495	177	7.13	2.61	38.0
30	2.0	0.739	264	7.39	2.63	56.2
60	2.0	1.516	541	7.16	2.74	111

Catalyst: MgCl₂·TiCl₄·DEP/PES/AlEt₃. Polymerization conditions: 60°C under atmospheric pressure, 2.0 mmol·L⁻¹ of PES and 6.0 mmol·L⁻¹ of AlEt₃ in 0.5 L of *n*-decane, 60 L·h⁻¹ of 1-butene feed rate.

(Table 2). These results suggest that the reported large activity enhancement (over three times) is caused by mutual interaction of all the components of MgCl₂·TiCl₄, DEP, AlEt₃, and PES.

Moreover, we investigated the influence of hydrogen addition on 1-butene polymerization. Hydrogen addition of 2 mol% decreased the intrinsic viscosity of the polymer from 2.62 to 1.23 dL/g and enhanced the activity 8.6 times, much higher than that in propene polymerization (3.3 times). Again, the stereospecificity of the polymer (23°C *n*-decane insoluble fraction) was not changed (Table 3).

A further investigation of 1-butene polymerization was carried out to find the reasons for the activity enhancement. We tried to compare the concentrations of the active sites [C*] in the presence and the absence of hydrogen by a kinetic study. Short-term 1-butene polymerization was performed by using MgCl₂·TiCl₄·DEP/AlEt₃/PES catalyst system at 60°C under atmospheric pressure for 10–60 s. Figure 1 shows the polymer yield and molecular weights measured by GPC as a function of the polymerization time. During the polymerization time studied (10–60 s), the polymer yield increased linearly with the polymerization time, showing that the polymerization rate is constant and the concentration of active sites remains constant during the polymerization time studied.

Table 4 lists the average molecular weights (Mn) and the polydisper-

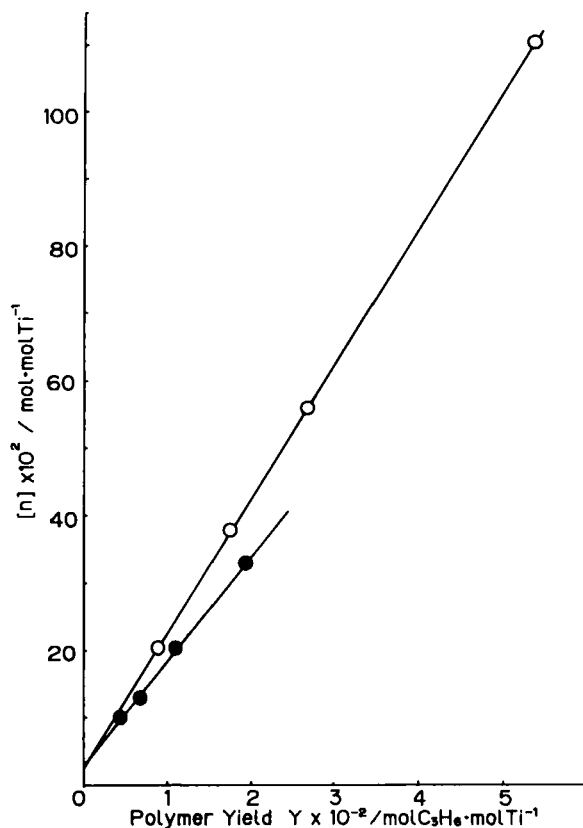


FIG. 2. Relation between the polymer yield, Y , and the number of polymer chains produced per mol of Ti $[n]$. ●, Hydrogen absence; ○, hydrogen presence.

TABLE 5. Kinetic Parameters in 1-Butene Polymerization

H_2 addition	Polymerization rate ($\text{mol} \cdot \text{mol Ti}^{-1} \cdot \text{s}^{-1}$)	$[\text{C}^*]$ (mol%)	K_p ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)
Yes	9.0	2.2	730
No	3.3	2.7	220

Catalyst: $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot \text{DEP/PES/AlEt}_3$. Polymerization conditions: 60°C under atmospheric pressure, $2.0 \text{ mmol} \cdot \text{L}^{-1}$ of PES and $6.0 \text{ mmol} \cdot \text{L}^{-1}$ of AlEt_3 in 0.5 L of n -decane, $60 \text{ L} \cdot \text{h}^{-1}$ of 1-butene feed rate, 2 mol% of H_2 content.

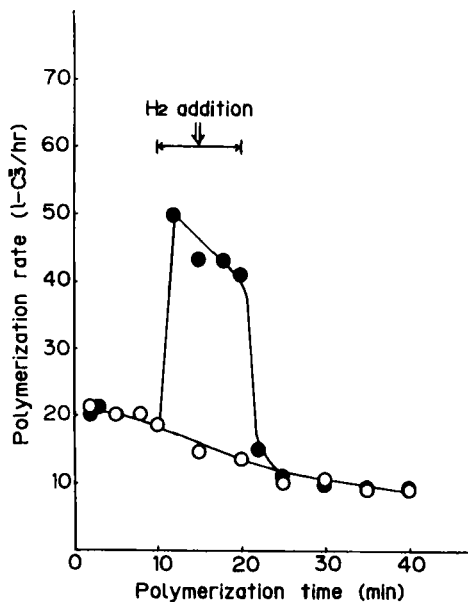


FIG. 3. Effect of hydrogen in propene consumption.

sity (M_w/M_n) of the obtained polymers at different polymerization times, together with the number of polymer chains produced per 1 mol of Ti atoms (n), calculated from the relation of polymer yield/ M_n . Figure 2 shows the relation between n and the polymer yield, which reveals that n increases linearly with polymer yield. The concentrations of active sites could be obtained from the intercept in Fig. 2, based on Eq. (1) [5].

$$n = [C^*] + (k_{tr} [C^*]/R) \cdot y \quad (1)$$

Where $[C^*]$ is the concentration of active sites, k_{tr} is the rate constant for the chain transfer reaction, y is the polymer yield, and R is the polymerization rate. On the other hand, R is expressed by Eq. (2).

$$R = k_p [M] [C^*] \quad (2)$$

Where k_p is the propagation rate constant and $[M]$ is the 1-butene concentration in solution ($[M] = 0.56 \text{ mol} \cdot \text{L}^{-1}$ at 1 atm and 60°C under the present experimental conditions). R was estimated from the slope in Fig. 1.

TABLE 6. Results of Ethene Polymerization

H ₂ conc. (mol%)	Yield (g)	(η) (dL/g)
0	37.9	27.2
2.0	35.2	8.33
3.3	33.7	6.74
8.0	28.5	4.80
13	26.6	4.31

Catalyst: MgCl₂·TiCl₄·DEP/PES/AlEt₃. Polymerization conditions: 60°C, 1 h under atmospheric pressure, 0.1 mmol·L⁻¹ Ti, 2.0 mmol·L⁻¹ of PES and 6.0 mmol·L⁻¹ of AlEt₃ in 0.5 L of *n*-decane, 60 L·h⁻¹ of ethene feed rate.

Kinetic parameters obtained are summarized in Table 5. These results show that the activity enhancement by hydrogen is attributable to the increase of k_p rather than the increase of $[C^*]$. And the same might be valid also for propene polymerization.

An additional result was illustrated in Fig. 3. After 15 min of propene polymerization, hydrogen was introduced into the system for 10 min together with propene, resulting in the polymerization rate increasing about 2.4 times. When the supply of hydrogen was stopped, the rate returned rapidly to the original level without hydrogen, supporting the previous conclusion that the reported enhancement is not due to the increase of the number of active sites.

On the other hand, unexpectedly, in ethene polymerization such enhancement could not be observed (Table 6), indicating that it occurred only for stereospecific or regiospecific polymerization. From the pre-described fact that the activity enhancement is observed in isospecific as well as aspecific polymerization independently from the stereospecificity, it would be associated to the regiospecific nature of the active sites.

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