

Study of activity enhancement by hydrogen in propylene polymerization using stopped-flow and conventional methods

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Abstract

The activity enhancement effect of hydrogen in propylene polymerization with a MgCl_2 -supported Ziegler catalyst was studied by using the stopped-flow polymerization method, by which a reaction can be conducted within an extremely short period (ca. 0.1 s). Kinetic study using this method suggested that the hydrogen did not affect the propagation rate constant and did not lead to the formation of new active sites. The results of the stopped-flow polymerization with a pre-treated catalyst indicated that activity enhancement by hydrogen did not take place in the region, under which hydrogen acts as a chain transfer agent and the reduction of the titanium species is believed to occur to produce dead sites. Slurry polymerization with prolonged polymerization time indicated that hydrogen affected both chain transfer reaction and activity enhancement, which may be due to the reactivation of the dormant sites by hydrogen. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: MgCl_2 -supported Ziegler catalyst; Hydrogen; Activity enhancement; Stopped-flow method; Dormant sites

1. Introduction

The effect of hydrogen on olefin polymerization using Ziegler–Natta catalysts has long been of commercial interest, because hydrogen has been used as a standard molecular weight modifier in industrial polyolefin production. In addition to acting as a powerful transfer agent, hydrogen is known to lead to activity enhancement. Several researchers demonstrated that the addition of hydrogen in olefin polymerization

caused a marked increase in the polymerization rate [1].

There are several distinct viewpoints on the essential action of the activity enhancement effect of hydrogen in propylene polymerization with supported Ziegler catalysts. These hypotheses primarily point to an increase in the propagation rate constant and the number of active sites concentration. Using the ^{14}C O radio-labelling method, Parsons and Al-Turki [2] showed that the number of active sites was increased significantly by the addition of hydrogen. Bukatov et al. [3], however, found that the introduction of hydrogen in propylene polymerization changed the values in the number of active sites as well as in the propagation rate constant, which were also determined by using

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^{14}CO for polymerization inhibition. A plausible explanation for the activating effect of hydrogen is that the regioirregular (2,1-) insertion of propylene into a growing chain leads to a species which is not active in regard to further polymerization and effectively remains as dormant sites until a chain transfer with hydrogen occurs [4–9]. It has also been suggested that the most probable event after a 2,1-insertion is chain transfer by monomer to give an allylic dormant structure, which may be reactivated by hydrogen [10,11]. Although several hypotheses have been put forth to explain the activity enhancing effect of hydrogen, there is not enough experimental evidence to reach a definite conclusion; therefore, the subject remains controversial.

In this study, the contribution to the elucidation of the activity enhancement effect of hydrogen in propylene polymerization with MgCl_2 -supported catalyst will be given in terms of the explanations mentioned above. Our approach is based mainly on the stopped-flow polymerization method, by which a reaction can be conducted within an extremely short period (ca. 0.1 s) [12]. Kinetic study using this method, combined with conventional slurry polymerization, is the most suitable approach in order to elucidate the activity enhancement effect of hydrogen.

2. Experimental

2.1. Catalyst and materials

Propylene (donated by Chisso) and H_2 (purchased from Nippon Sanso, 99.9999%) were used without further purification. Triethylaluminum (TEA, donated by Tosoh Akzo) was used as a heptane solution. Heptane was purified by passing it through a molecular sieves $13 \times$ column.

The highly active MgCl_2 -supported catalyst used in this study was prepared by a similar procedure that has been described elsewhere [13,14]. The Ti content of the catalyst was 0.40

mmol-Ti/g-cat. A pre-treated catalyst was prepared by the reaction of the catalyst with TEA in heptane at 30°C for 5 min.

2.2. Stopped-flow polymerization of propylene and estimation of kinetic parameters

The stopped-flow polymerization of propylene and the estimation of kinetic parameters were performed according to a method used elsewhere [12,15]. Propylene polymerization was performed with a catalyst (1.2 g) and TEA (14 mmol, Al/Ti mole ratio = 30) in heptane at 30°C for 0.05–0.20 s. The propagation rate constant (k_p) and active sites concentration ($[\text{C}^*]$) were determined by the following equations [12]:

$$\bar{M}_n = M_0 \frac{k_p [\text{M}] t}{1 + k_{tr} t} \quad (1)$$

$$Y = k_p [\text{M}] [\text{C}^*] t \quad (2)$$

where \bar{M}_n , M_0 , $[\text{M}]$, Y , t , and k_{tr} are the number-average molecular weight of the polymer, the molecular weight of the monomer, the monomer concentration, the polymer yield, the polymerization time, and the rate constant of the transfer, respectively.

For polymerization with a pre-treated catalyst, catalyst pre-treatment was done with TEA for 5 min at 30°C in one of the vessels, and only the heptane that had been placed in another vessel was saturated with propylene.

2.3. Slurry polymerization of propylene

The slurry polymerization of propylene (1 kgf/cm^2) was performed with the MgCl_2 -supported Ziegler catalyst (0.10 g) and TEA ($[\text{Al}] = 20 \text{ mmol/l}$, Al/Ti molar ratio = 100) in heptane (200 ml) at 60°C for 30 min. The desired amount of co-catalyst was added into the propylene-saturated heptane containing the catalyst, where polymerization had begun. 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) as much as 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 polymerization, the reaction was quenched with ethanol containing 20 vol.% of conc. HCl, and then the polymer obtained was washed with a large amount of distilled water and dried in vacuo.

The polymerization of propylene (8 kgf/cm²) was also performed in a 1-l glass autoclave reactor (TEM-V1000N, Taiatsu Techno) with the MgCl₂-supported Ziegler catalyst (83 mg) and TEA ([Al] = 2.0 mmol/l, Al/Ti molar ratio = 300) in heptane (500 ml) at 70°C for 60 min.

2.4. Measurements

The molecular weight of the polymer that was obtained via stopped-flow polymerization was determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (TSK-GEL GMHHR-M and TSK-GEL G2000HHR, Tosoh) at 140°C using *o*-dichlorobenzene as a solvent. A polystyrene gel column (Jordi-Gel DVB Mixed Bed) was used to determine molecular weight and the distribution of polymer obtained through slurry polymerization. ¹³C NMR spectra were recorded on a Varian Gemini-300 spectrometer at 120°C on 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

In previous studies by the authors, the stopped-flow polymerization method was used

to study chain-transfer reaction by hydrogen in the initial stage of propylene polymerization [15–17]. This research yielded significant data on the effect of hydrogen, particularly in regard to the chain transfer reaction by atomic hydrogen formed by dissociation of the hydrogen molecule. The authors have only focused on chain-transfer reaction mechanism with hydrogen, while they have paid less attention to the activity enhancement effect of hydrogen in olefin polymerization.

In this study, the results of the stopped-flow polymerization of propylene in the presence or absence of hydrogen were analyzed in terms of the activity enhancement effect of hydrogen. The addition of hydrogen had no apparent effect on either the yield or the molecular weight of the resulting polymer, as shown in Fig. 1a and b. No difference was observed even when higher hydrogen pressure (4 kgf/cm²) was introduced into the polymerization system. In all of the examples, the polymer yield and molecular weight were apparently proportional to the polymerization time, indicating that the nature of the active sites on the catalyst was constant and that the chain transfer and termination reactions were negligible regardless of the presence of hydrogen. The kinetic parameters, the propagation rate constant (k_p), and the concentration of active sites ($[C^*]$), were obtained from the values of the polymer yield and the number-average molecular weight of polymer using Eqs. (1) and (2). As can be seen in Table 1, the values of k_p and $[C^*]$ are almost the same regardless of the presence of hydrogen. On the basis of the result, the previous hypothesis in regard to an increase in k_p is inaccurate as a reason of the activity enhancement effect by hydrogen. No influence of hydrogen on the value of $[C^*]$ indicates that hydrogen does not lead to the formation of new active sites.

In propylene polymerization, a MgCl₂-supported Ziegler catalyst is subject to rapid decay due to the deactivation of the active sites by interaction with alkylaluminium, at which further reduction of Ti³⁺ species occurs to produce

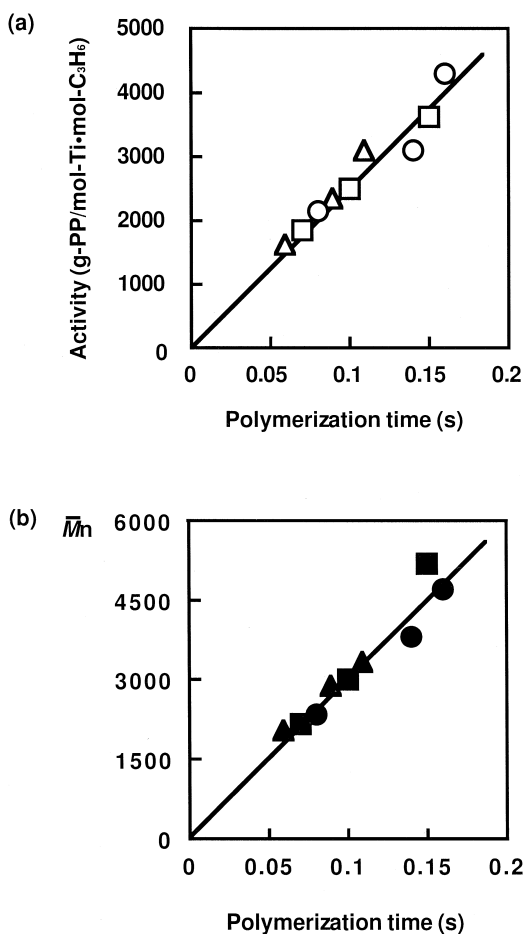


Fig. 1. Results of the stopped-flow polymerization with the MgCl_2 -supported catalyst in the presence ($\blacktriangle, \triangle$: 1 kgf/cm²; \blacksquare, \square : 4 kgf/cm²) or absence (\bullet, \circ) of hydrogen. Dependence of activity (a) and \bar{M}_n (b) on polymerization time.

a lower oxidation state having no activity for propylene polymerization [18–20]. From this perspective, the MgCl_2 -supported Ziegler catalyst came into contact with TEA at 30°C for 5

Table 1
Kinetic parameters for propylene polymerization^a

Hydrogen	k_p^b (1 mol ⁻¹ s ⁻¹)	$[\text{C}^*]^b$ (mol%)
Absent	1150	11
Present (4 kgf/cm ²)	1100	11

^aThe polymerization was carried out using the stopped-flow technique.

^b $[\text{C}^*]$ and k_p were estimated by Eqs. (1) and (2).

min, followed by stopped-flow polymerization. The significant deactivating behavior was apparently observed as in Fig. 2, when catalyst pre-treatment was performed with TEA. The experiment, therefore, could be regarded as polymerization with a pre-treated catalyst, which certainly contains the dead sites produced by reaction with TEA. The molecular weight of the obtained polymer decreased in the presence of hydrogen, even though the polymer yield was not affected (Fig. 3). This indicates that hydrogen acts as a chain-transfer agent in propylene polymerization using the catalyst that was modified by pre-treatment with TEA. There were, however, no activity enhancement effect of hydrogen, where the reduction of the titanium species is believed to occur to produce the dead sites for polymerization. This indicates that the reactivation of the dead sites by hydrogen does not occur in the region, and that this is not applicable as the reason of the activity enhancement by hydrogen.

The effect of hydrogen was examined using conventional slurry polymerization for the purpose of obtaining a better understanding of the mechanism of the activity enhancement effect of hydrogen in relation to the existence of dormant sites. The prolonged polymerization time

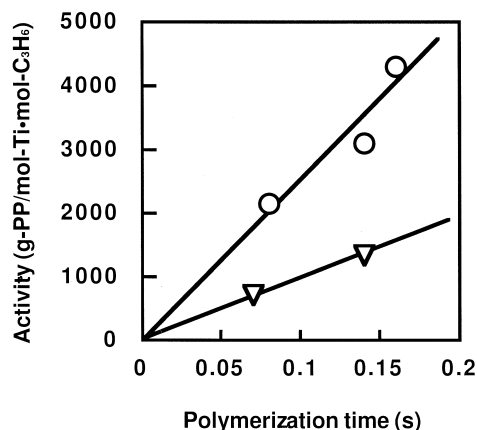


Fig. 2. Dependence of activity on polymerization time. The stopped-flow polymerization was carried out with the MgCl_2 -supported catalyst (\circ) or the pre-treated catalyst (∇) in the absence of hydrogen.

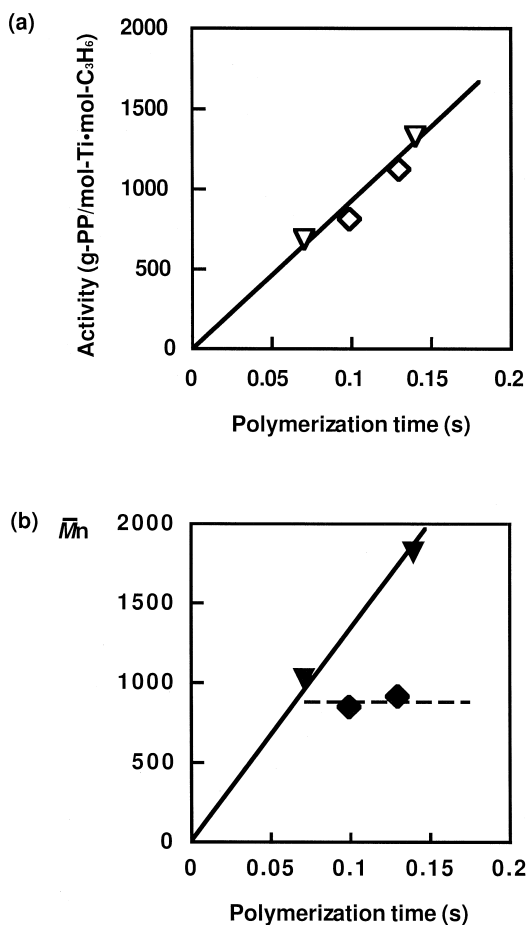


Fig. 3. Results of the stopped-flow polymerization with the pre-treated catalyst in the presence (◆,◇: 1 kgf/cm²) or absence (▼,▽) of hydrogen. Dependence of activity (a) and \bar{M}_n (b) on polymerization time.

is thought to induce the formation of dormant sites in addition to the deactivation of active sites. The slurry polymerization of propylene (1 kgf/cm²) was performed using the MgCl₂-supported Ziegler catalyst with TEA at 60°C for 30 min in the presence and absence of hydrogen, and the polymerization rate was measured by evaluating monomer consumption. The solid line in Fig. 4 shows the polymerization curve without hydrogen, suggesting that the initial activity of polymerization with TEA was very high, followed by a drastic decay. It may be that the titanium species on the catalyst are activated at the beginning of polymerization, followed by a

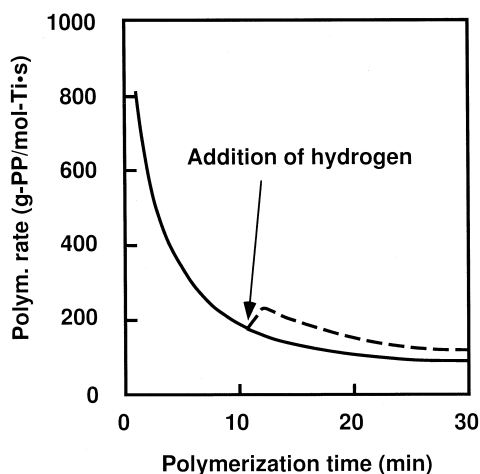


Fig. 4. Relationship between polymerization time and polymerization rate with the MgCl₂-supported Ziegler catalyst. The solid line indicates the result of slurry polymerization of propylene (1 kgf/cm²) without hydrogen. The dotted line indicates the result when hydrogen (5 ml) was introduced to the system after the polymerization for 10 min.

progressive reduction in titanium species with polymerization time. After 10 min, a small amount of hydrogen (5 ml) was introduced into the polymerization system, which caused a rapid increase of the polymerization rate, as can be seen in the dotted line in Fig. 4. Under the same conditions, the slurry polymerization of propylene was performed in the presence of hydrogen (10 ml/min), resulting in a slight increase in polymerization activity and a decrease in the molecular weight of the obtained polypropylene (Table 2). The polymerization of propylene (8 kgf/cm²) 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 increased considerably through the addi-

Table 2
Slurry polymerization of propylene (1 kgf/cm²)

Condition	Activity (kg-PP/mol-Ti)	\bar{M}_n^a	\bar{M}_w / \bar{M}_n^a
Without H ₂	350	6800	7.5
Introduction of H ₂ (5 ml)	370	6200	6.7
With H ₂ (10 ml/min)	390	6100	5.1

^aDetermined by GPC.

Table 3
Slurry polymerization of propylene (8 kgf/cm²)

Condition	Activity (kg-PP/mol-Ti)	\bar{M}_n^a	\bar{M}_w / \bar{M}_n^a
Without H ₂	8000	40000	8.8
With H ₂ (100 ml)	12200	25000	5.2

^aDetermined by GPC.

tion of hydrogen to the polymerization system, whereas the value of the molecular weight decreased. This indicates that hydrogen significantly affects both the chain transfer reaction and activity enhancement, which may be due to the reactivation of the dormant sites by hydrogen.

The activity enhancement effect of hydrogen in propylene polymerization with a MgCl₂-supported catalyst was studied in terms of four likely explanations: (1) an increase in the propagation rate constant, (2) the formation of new active sites, (3) the reactivation of dead sites, and (4) the reactivation of dormant sites. The results using the stopped-flow polymerization method showed that the first three hypotheses could not be employed in this case. The results from slurry polymerization indicated that hydrogen apparently affected activity enhancement, where dormant sites were believed to be present. Therefore, it was concluded that the only feasible reason for the activity enhancement was last one—i.e., the reactivation of the dormant sites by hydrogen.

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