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| Author(s)    | Taniike, Toshiaki; Wada, Toru; Kouzai, Iku; Takahashi, Shougo; Terano, Minoru  |
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| Description  |  |

**Role of Dispersion State of Ti Species in Deactivation of MgCl<sub>2</sub>-Supported  
Ziegler-Natta Catalysts**

Toshiaki Taniike, Toru Wada, Iku Kouzai, Shogo Takahashi, Minoru Terano\*

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1  
Asahidai, Nomi, Ishikawa, 923-1292, Japan

*Corresponding author*

Prof. Dr. Minoru Terano

TEL: +81-761-51-1620, FAX: +81-761-51-1625, E-mail: [terano@jaist.ac.jp](mailto:terano@jaist.ac.jp)

## **Running Head:** Role of Ti Dispersion State in Catalyst Deactivation

### **Abstract**

Deactivation behaviors of  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts with molecularly dispersed  $\text{TiCl}_3$  were investigated to clarify the role of the dispersion state of the Ti species in the deactivation of  $\text{MgCl}_2$ -supported Ziegler-Natta (ZN) catalysts for propylene and ethylene polymerization. The propylene and ethylene polymerization activities of clustered Ti species supported on  $\text{MgCl}_2$  were about one tenth of those of isolated Ti species, indicative of a significance of the aggregation of Ti species in the deactivation of ZN catalysts for olefin polymerization. Moreover, the time-course depression of the monomer consumption for the clustered Ti species was slower than that for the isolated Ti species in propylene polymerization, while the dispersion state hardly affected the depression rate in ethylene polymerization. The reduction rate of the Ti species was concluded as important for the time-course depression of propylene consumption, while ethylene polymerization was insensitive to the oxidation state of the Ti species.

## Introduction

MgCl<sub>2</sub>-supported Ziegler-Natta (ZN) catalysts have played a dominant role in the industrial polyolefin production.<sup>1</sup> Enormous scientific researches have been accumulated on the ZN catalysts with the aim of getting better understanding for all the aspects of olefin polymerization catalysis such as the polymerization mechanism, active site structure, and etc. However, only a limited attention has been paid to the deactivation behavior of the ZN catalysts and to its mechanism, even though it is one of the most important catalytic features. Deactivation of the ZN catalysts has been generally defined as a time-course depression of olefin monomer consumption during polymerization, and is normally a phenomenon in the time scale of hours.<sup>2</sup> Several mechanisms have been proposed so far, which are briefly reviewed in the introduction.

Keii et al. estimated an active site concentration [C\*] and a propagation rate constant  $k_p$  as a function of polymerization time for a TiCl<sub>4</sub>/MgCl<sub>2</sub> catalyst by means of a CO quenching technique. They found that a decrease of [C\*], *i.e.* deactivation of the active sites, was the main reason of the decay, while  $k_p$  was rather kept unchanged in the absence of donors.<sup>3</sup> For the deactivation of each active site, the role of the oxidation state of Ti species has been believed as crucial. Generally, in the production of polyolefin with the ZN catalysts, an alkylaluminum activator is required to convert TiCl<sub>4</sub> precursor that is supported on MgCl<sub>2</sub> into active sites through alkylation and reduction of TiCl<sub>4</sub>.<sup>1</sup> The oxidation state of Ti species varies from IV to II during polymerization. Soga et al. concluded that both of Ti<sup>2+</sup> and Ti<sup>3+</sup> species were active for ethylene polymerization but  $\alpha$ -olefins including propylene could polymerize only with Ti<sup>3+</sup> species.<sup>4</sup> Kashiwa et al. found that a completely deactivated TiCl<sub>4</sub>/MgCl<sub>2</sub> catalyst for propylene polymerization through aging with AlEt<sub>3</sub> for 1 h at 60°C could be reactivated with an introduction of

various Cl-based oxidants (for instance,  $\text{Cl}_2$ ).<sup>5</sup> They indicated that the formation of  $\text{Ti}^{2+}$ , called as an over-reduction, was a major reason of the deactivation of the active sites in ZN olefin polymerization. On the contrary, Albizzati et al. reported that a  $\text{MgCl}_2$ -supported  $\eta^6$ -Benzene $\text{Ti}(\text{II})\text{Al}_2\text{Cl}_8$  complex was quite active for propylene polymerization.<sup>6</sup> Though the supported complex including benzene and  $\text{Al}_2\text{Cl}_8$  might not be a good active site model for real  $\text{Ti}^{2+}$  species produced by the over-reduction of  $\text{TiCl}_4$ , the over-reduction of the Ti species must not be the sole reason of the deactivation. Another source of the active sites deactivation is aggregation of Ti species which proceeds in parallel with the reduction during polymerization, leading to a decrease in the active site concentration. Several electron spin resonance (ESR) studies revealed that a contact of  $\text{TiCl}_4/\text{MgCl}_2$  with alkylaluminum produced a large amount of ESR-silent  $\text{Ti}^{3+}$  species, assigned as clustered  $\text{Ti}^{3+}$  species.<sup>7-10</sup> Recently, Tregubov et al. reported that the dispersion state of the Ti species was vital for the ethylene polymerization activity.<sup>11</sup>

Aside from the said chemical deactivation of the active sites, physical origins were also proposed for the decay of the ZN catalysts. One famous proposal is related to the inhibition of monomer diffusion from reactor medium to active sites by encapsulation of the active sites with growing polymer layers, so called a filter effect.<sup>2</sup> However, Keii et al. found that a contact of a  $\text{TiCl}_4/\text{MgCl}_2$  catalyst with  $\text{AlEt}_3$  in the absence or in the presence of propylene similarly promoted the decay of subsequent monomer consumption, claiming a dominant role of the chemical deactivation of the active sites rather than the inhibited monomer diffusion at least for propylene polymerization.<sup>3</sup> On the other hand, it is certain that the time-course change of the monomer consumption, namely polymerization kinetics, is deeply related to the morphology development of polymer/catalyst particles. Generally, polymer chains growing from active sites fill catalyst pores or channels to produce a stress,

resulting in disintegration of catalyst particles. Ti species located deep inside catalyst particles and unable to be in contact with alkylaluminum at an early stage of polymerization get exposed in the course of polymerization, and lead to new active sites.<sup>2</sup> The decay curve of monomer consumption thus results from the balance between the active sites deactivation and morphology-driven formation of new active sites. Tait et al. found that the kinetic profile of the ZN catalysts was strongly influenced by the catalyst synthesis route.<sup>12</sup> We have also proposed that the spatial distribution of Ti species inside catalyst particles was strongly dependent on the synthetic procedure to diverse kinetic profiles and morphology developments among differently prepared ZN catalysts.<sup>13</sup>

In summary, three factors (the over-reduction and aggregation of Ti species, and the disintegration of catalyst particles) are believed to collaborate in polymerization with MgCl<sub>2</sub>-supported ZN catalysts in order to give a specific decay curve of monomer consumption. It is essential to study these three factors individually for investigating the deactivation behavior of the ZN catalysts. Recently we have prepared a TiCl<sub>3</sub>/MgCl<sub>2</sub> model catalyst from a TiCl<sub>3</sub>·3C<sub>5</sub>H<sub>5</sub>N molecular precursor,<sup>14-16</sup> where TiCl<sub>3</sub> is molecularly dispersed on the MgCl<sub>2</sub> surface. In this model catalyst, the dispersion state of TiCl<sub>3</sub> is precisely controllable by varying the Ti content in the catalyst, where a lower content leads to more isolated Ti species, while a higher content gives more aggregated Ti species. An initially-determined dispersion state of the Ti species is believed to be maintained during polymerization since TiCl<sub>3</sub> much more strongly adsorbs on MgCl<sub>2</sub> and hardly migrates on the surface during polymerization, whereas TiCl<sub>4</sub> is rather mobile on the surface and bound to reduced Ti species to cause the aggregation of Ti species. Moreover, TiCl<sub>3</sub> is supported on the exposed surface of MgCl<sub>2</sub> without breaking or reconstructing the original morphology of MgCl<sub>2</sub>, plausibly making the contribution from the disintegration of the

catalyst particles to the decay curves of the catalysts rather negligible. Thus, the novel  $\text{TiCl}_3/\text{MgCl}_2$  model catalyst allowed us to investigate the influences of the dispersion state and reduction of the Ti species separately on the deactivation behavior of  $\text{MgCl}_2$ -supported Ziegler-Natta catalysts.

The deactivation behaviors of the  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts having an “isolated” or “clustered” Ti species were acquired for propylene and ethylene polymerization in this article. Both the aggregation and reduction of the Ti species were found to be important for the depression of the propylene polymerization activity, while the ethylene polymerization activity was only sensitive for the aggregation.

## **Experimental part**

### *Materials*

Dehydration of heptane was performed by passing through a column filled with molecular sieve 13X. Pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) was dried with molecular sieve 13X. Propylene, ethylene and nitrogen of research grade,  $\text{MgCl}_2$  ( $65.1 \text{ m}^2 \cdot \text{g}^{-1}$ ) and aluminum-free T- $\text{TiCl}_3$  (both donated by Toho Titanium Co.), and  $\text{AlEt}_2\text{Cl}$  and  $\text{AlEt}_3$  (both donated by Tosoh Finechem Co.) were used without further purification.

### *Synthesis of $\text{TiCl}_3/\text{MgCl}_2$ model catalysts*

Preparation of the  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts was conducted according to the previously reported procedure<sup>14-16</sup> T- $\text{TiCl}_3$  (4.0 g) and  $\text{C}_5\text{H}_5\text{N}$  (20 ml) were mixed vigorously in nitrogen atmosphere for 8 h at  $140^\circ\text{C}$ . The mixture was washed adequately with heptane and dried in vacuo to obtain  $\text{TiCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$  as greenish fine powder. The measured amounts of  $\text{MgCl}_2$  and the  $\text{TiCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$  complex were placed in a flask under

nitrogen. Heptane solution of  $\text{AlEt}_2\text{Cl}$  ( $\text{Al/Ti} = 78 \text{ mol}\cdot\text{mol}^{-1}$ ) was introduced into the flask and stirred at room temperature for 3 h, then washed adequately with heptane to obtain the catalyst. The interaction between  $\text{TiCl}_3\cdot 3\text{C}_5\text{H}_5\text{N}$  and  $\text{AlEt}_2\text{Cl}$  is believed to transform  $\text{TiCl}_3\cdot 3\text{C}_5\text{H}_5\text{N}$  into some partly soluble or mobile species through a removal of the Py ligands by  $\text{AlEt}_2\text{Cl}$  so as to disperse  $\text{TiCl}_3$  units on  $\text{MgCl}_2$  surface at a molecular level. The Ti contents ranged from 0.004-1.3 wt.-% were determined by titration.

#### *Semi-batch slurry polymerization*

A 500 ml glass flask with a magnetic stirrer was filled with a measured volume of heptane kept at  $30^\circ\text{C}$ . Monomer gas was saturated in heptane at 0.015-0.020 MPa above the atmospheric pressure, and then  $\text{AlEt}_3$  was introduced, observing the monomer flow with a mass flow meter (Kofloc Model 3100). After the stabilization of the baseline in the flow meter, a measured amount of catalyst slurry (the total liquid volume was 300 ml) was injected to start the polymerization. During polymerization, the propylene or ethylene pressure was kept at constant within the above range and the monomer consumption was recorded on line using a mass flow meter throughout the polymerization for 2 h. The polymerization was terminated by adding 20 ml of ethanol containing 20 vol.-% of HCl. The amount of the injected catalysts was adjusted in order to produce around 10 g of polymers for all the conditions. The Al concentration was varied from 6.25 to  $125 \text{ mol}\cdot\text{L}^{-1}$ .

## **Results and discussion**

In our previous paper,<sup>16</sup> the dispersion state of Ti species in the  $\text{TiCl}_3/\text{MgCl}_2$  model catalyst was controlled by varying the Ti content to investigate its influences on the propylene



polymerization performance. The results for the catalyst activity and stereoregularity of the made polypropylenes are summarized in Figure 1. The stereoregularity was increased with increasing the Ti content over 0.1-1.3 wt.-%, while it became constant below 0.1 wt.-%. The increase of the catalyst stereospecificity at a higher Ti content came from the formation of clustered Ti species, which generally have a higher stereospecificity than an isolated Ti species. The convergence of the stereoregularity below 0.1 wt.-%, on the other hand, indicated the loss of the Ti-Ti interaction, *i.e.* each Ti species existed on the MgCl<sub>2</sub> surface in an isolated manner. The propylene polymerization activity of the model catalyst with 0.08 wt.-% of the Ti content was *ca.* 10 times higher than that of the catalyst with 0.9 wt.-%, clearly indicating that the aggregation of the Ti species significantly promoted the depression of the monomer consumption plausibly due to a much lower active site concentration. It is also notable that both the catalysts gave poorly crystallizable polypropylenes, and therefore the filter effect was considered to be minimized.

Hereafter, two catalysts with the Ti content of 0.08 and 0.90 wt.-% (Cat-0.08 and Cat-0.90) were employed as representatives of the catalysts including “isolated” and “clustered” Ti species in order to investigate the deactivation behaviors for propylene and ethylene polymerizations. The shapes of the kinetic profiles were quantified and compared by four parameters (Tables 1 and 2);  $R_{p,ave}$  and  $R_{p,max}$  respectively as average and maximum instantaneous consumptions of monomers,  $t(R_{p,max})$  as the time when the activity reaches the maximum value, and  $R_{p,max}/R_p(2\text{ h})$  as a decay index on average. Figure 2 shows the kinetic profiles of propylene polymerization for Cat-0.08 and Cat-0.90 with the Al concentration of 12.5 mmol/L<sup>-1</sup>.  $R_p$  of Cat-0.08 was around 10 times higher than that of Cat-0.90, indicating that the clustering of the Ti species gave a significant effect to the

total activity due to decrease in the number of surface Ti species being able to react with alkylaluminum. Cat-0.08 exhibited faster increase and depression of the monomer consumption, respectively quantified by  $t(R_{p,max})$  and  $R_{p,max}/R_p(2\text{ h})$ , than Cat-0.90.  $t(R_{p,max})$  and  $R_{p,max}/R_p(2\text{ h})$  for propylene polymerization were plotted as a function of the Al concentration in Figures 3 and 4. The increase in the Al concentration made  $t(R_{p,max})$  smaller and  $R_{p,max}/R_p(2\text{ h})$  larger, similarly for the two catalysts. As was already described, the dispersion state of the Ti species for the  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts was believed to hardly change during the polymerization, and therefore the time-course depression of the monomer consumption was considered to purely reflect the progress of the over-reduction of the Ti species by  $\text{AlEt}_3$ . The difference in the activation and deactivation rates between the two catalysts suggested that the dispersion state of the Ti species affected not only the absolute activity but also the reaction rate of the Ti species with  $\text{AlEt}_3$ . The reason of the measured slower activation and deactivation for the clustered Ti species was safely explainable, as follows. In the clustered Ti species, one Ti ion can exchange its electron with neighboring Ti ion through bridging Cl ions. For instance, a deactivated active site ( $\text{Ti}^{2+}$ ) as a result of the over-reduction can be reactivated by transferring its excess electron to neighboring  $\text{Ti}^{3+}$  species, where the neighboring Ti species works as an oxidant. In other words, Ti species belonging to a cluster is able to pool the surplus electron to slow down the rate of the average reduction rate in the cluster. This mechanism resembles the reactivation of a  $\text{TiCl}_4/\text{MgCl}_2$  catalyst by the addition of Cl-based oxidants reported by Kashiwa et al.<sup>5</sup> It is also considered that Ti ions in a cluster have a larger coordination number in terms of Cl ions than isolated Ti ions, and therefore a larger amount of Cl should be removed from the clustered Ti species than from the isolated Ti species in order to prepare a vacant site for monomer coordination that is

essential to make an active site. Thus, the activation of the clustered Ti species should be slower.

The kinetic profiles of ethylene polymerization for the two catalysts with the Al concentration of  $12.5 \text{ mmol/L}^{-1}$  are shown in Figure 5. The dependences of  $t(R_{p,\text{max}})$  and  $R_{p,\text{max}}/R_p(2 \text{ h})$  on the Al concentration are plotted in Figures 6 and 7.  $R_p$  of Cat-0.08 exceeded that of Cat-0.90 by an order of magnitude in the same fashion as for propylene polymerization (Tables 1 and 2), again indicating a significance of the aggregation for the catalyst activity. As can be seen from  $t(R_{p,\text{max}})$  and  $R_{p,\text{max}}/R_p(2 \text{ h})$  in Tables 1 and 2, the activation and deactivation for the ethylene polymerization were much slower than those for propylene polymerization. It was previously reported that the most active oxidation state of Ti species for ethylene polymerization was II,<sup>17</sup> implying a slower activation.  $t(R_{p,\text{max}})$  were about 30-50 min for ethylene polymerization, while the propylene consumption rate already became 10-20% of the maximum value at the timing. Moreover, there was no drastic decay of the activity even after 2 h of polymerization on the contrary to the case of propylene polymerization, indicative of the insensitivity of ethylene polymerization to the oxidation state of Ti species as Kashiwa et al. and Tregubov et al. pointed out. It is also taken into consideration that the diffusion of ethylene must play an important role based on the following two reasons: i) the crystallinity of the produced polyethylenes was not low for the two catalysts, and ii) the solubility of ethylene is much lower than that of propylene, while the reactivity of ethylene is much larger than that of propylene.<sup>18</sup> Thus, it was not easy to give a clear explanation to the deactivation behavior of the catalysts for ethylene polymerization. However, the importance of the aggregation and the immateriality of the over-reduction of Ti species were safely concluded for the depression of the ethylene polymerization activity.

## **Conclusion**

The catalyst deactivation behaviors were investigated for propylene and ethylene polymerization using  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts. The advantage of the  $\text{TiCl}_3/\text{MgCl}_2$  model catalyst, namely, the controlled dispersion state of Ti species, enabled us to study in detail the origin of the deactivation of active sites in  $\text{MgCl}_2$ -supported Ziegler-Natta catalysts. The aggregation of the Ti species significantly reduced both the propylene and ethylene polymerization activities, and was identified as one of the major deactivation mechanisms. The time-course depression of the monomer consumption which arose from the over-reduction of Ti species was prominent for propylene polymerization, while it was subtle for ethylene polymerization. The role of the aggregation and over-reduction of Ti species were successfully understood in relation to the deactivation of  $\text{MgCl}_2$ -supported Ziegler-Natta catalysts, which is expected to be valuable for the design of highly active industrial olefin polymerization catalysts.

## ***Acknowledgement***

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### Figure/Scheme Captions

Figure 1. Stereoregularity (●) of the polypropylenes and activity (○) with respect to the Ti content. Propylene polymerization was conducted under normal pressure at 30°C in heptane with 12.5 mmol·L<sup>-1</sup> of AlEt<sub>3</sub> for 30 min.

Figure 2. (a) Kinetic profiles of propylene polymerization with Cat-0.08 (●) and Cat-0.90 (○), and (b) the magnification of the initial stage of the polymerization. The Al concentration was 12.5 mmol·L<sup>-1</sup>.

Figure 3.  $t(R_{p,max})$  vs. the Al concentration for propylene polymerization with Cat-0.08 (■) and Cat-0.90 (□)

Figure 4.  $R_{p,max}/R_p(2\text{ h})$  vs. the Al concentration for propylene polymerization with Cat-0.08 (■) and Cat-0.90 (□)

Figure 5. (a) Kinetic profiles of ethylene polymerization with Cat-0.08 (●) and Cat-0.90 (○), and (b) the magnification of the initial stage of the polymerization. The Al concentration was 12.5 mmol·L<sup>-1</sup>.

Figure 6.  $t(R_{p,max})$  vs. the Al concentration for ethylene polymerization with Cat-0.08 (■) and Cat-0.90 (□).

Figure 7.  $R_{p,max}/R_p(2\text{ h})$  vs. the Al concentration for ethylene polymerization with Cat-0.08 (■) and Cat-0.90 (□)

Table 1. Kinetic parameters of propylene polymerization with the  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts.

| Ti contents / wt.-%   | 0.08 |      |      |      | 0.90 |      |      |      |
|---|------|------|------|------|------|------|------|------|
|   | 6.25 | 12.5 | 62.5 | 125  | 6.25 | 12.5 | 62.5 | 125  |
| $R_{p,ave}^a \times 10^{-3} / \text{kg-C}_3\text{H}_6 \cdot \text{mol-Ti}^{-1} \cdot \text{h}^{-1}$ | 1.4  | 1.2  | 0.94 | 0.94 | 0.16 | 0.14 | 0.11 | 0.10 |
| $R_{p,max}^a \times 10^{-3} / \text{kg-C}_3\text{H}_6 \cdot \text{mol-Ti}^{-1} \cdot \text{h}^{-1}$ | 5.4  | 5.1  | 4.3  | 4.5  | 0.44 | 0.43 | 0.38 | 0.34 |
| $t(R_{p,max}) / \text{min}^b$   | 5.9  | 5.3  | 4.2  | 3.3  | 9.2  | 8.4  | 7.3  | 6.6  |
| $R_{p,max}/R_p(2 \text{ h})^b$  | 11   | 9.9  | 13   | 15   | 6.1  | 6.9  | 7.5  | 9.1  |

<sup>a</sup> Averaged and maximum instantaneous consumptions of propylene.

<sup>b</sup> Time when the activity reaches the maximum value, and decay index on average.



Table 2. Kinetic parameters of ethylene polymerization with the  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts.

| Ti contents / wt.-%   | 0.08 |      |      |     | 0.90 |      |      |      |
|---|------|------|------|-----|------|------|------|------|
|   | 6.25 | 12.5 | 62.5 | 125 | 6.25 | 12.5 | 62.5 | 125  |
| $R_{p,ave} \times 10^{-3} / \text{kg-C}_2\text{H}_4 \cdot \text{mol-Ti}^{-1} \cdot \text{h}^{-1}$ | 4.9  | 5.7  | 6.6  | 6.2 | 0.52 | 0.64 | 0.70 | 0.64 |
| $R_{p,max} \times 10^{-3} / \text{kg-C}_2\text{H}_4 \cdot \text{mol-Ti}^{-1} \cdot \text{h}^{-1}$ | 6.0  | 7.1  | 8.3  | 8.1 | 0.64 | 0.78 | 0.88 | 0.83 |
| $t(R_{p,max}) / \text{min}$   | 55   | 47   | 37   | 24  | 64   | 41   | 32   | 21   |
| $R_{p,max}/R_p(2 \text{ h})$  | 1.2  | 1.3  | 1.5  | 1.5 | 1.3  | 1.2  | 1.3  | 1.6  |

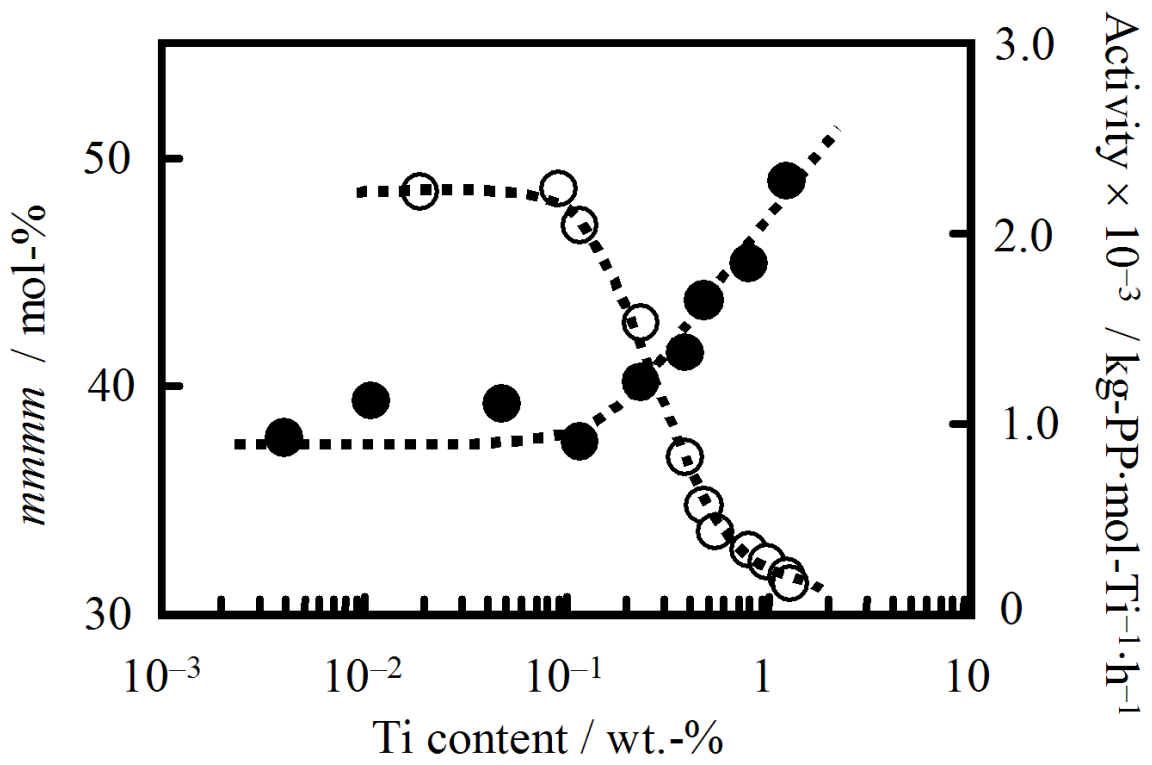


Figure 1. Taniike et al.

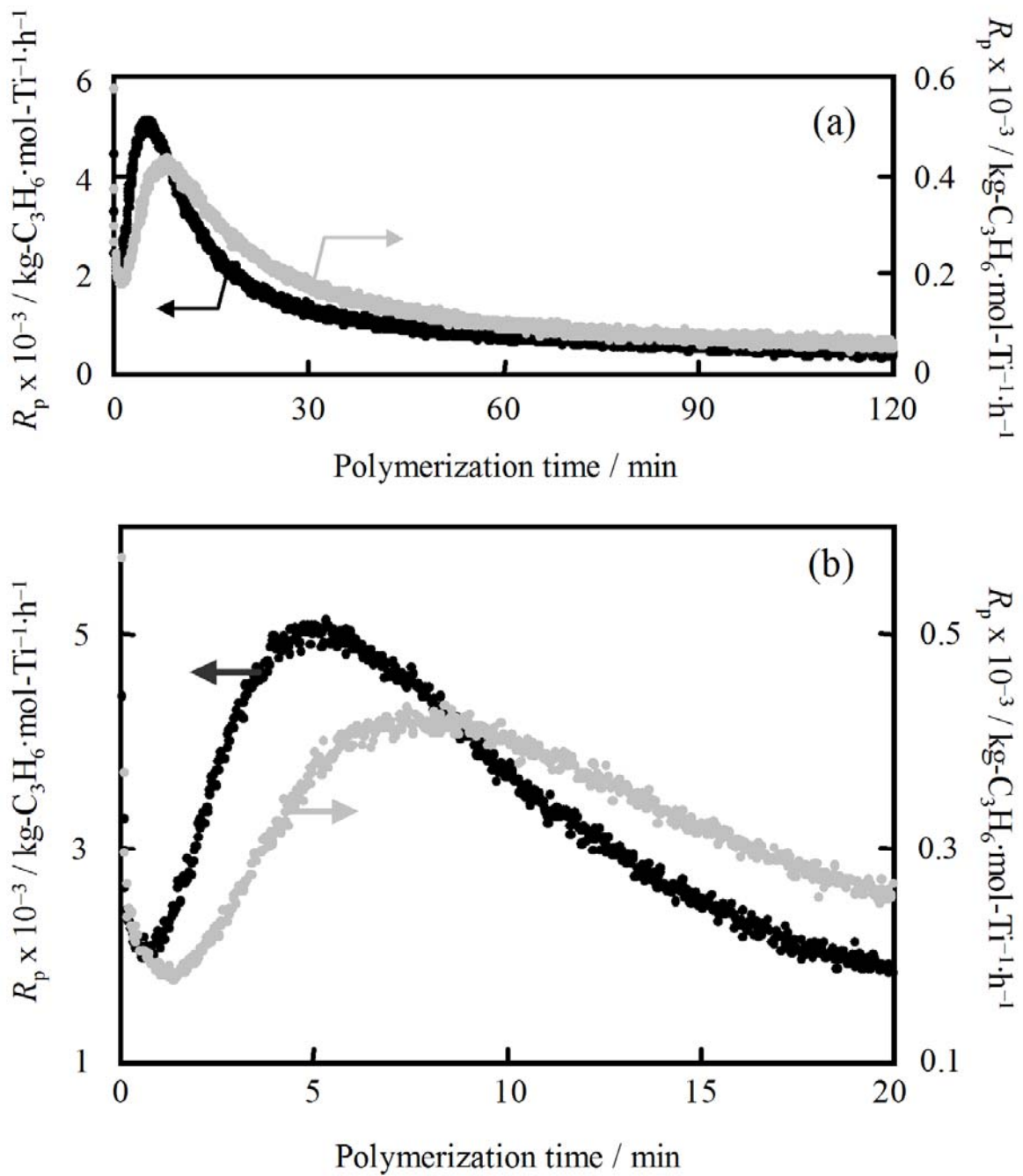


Figure 2. Taniike et al.

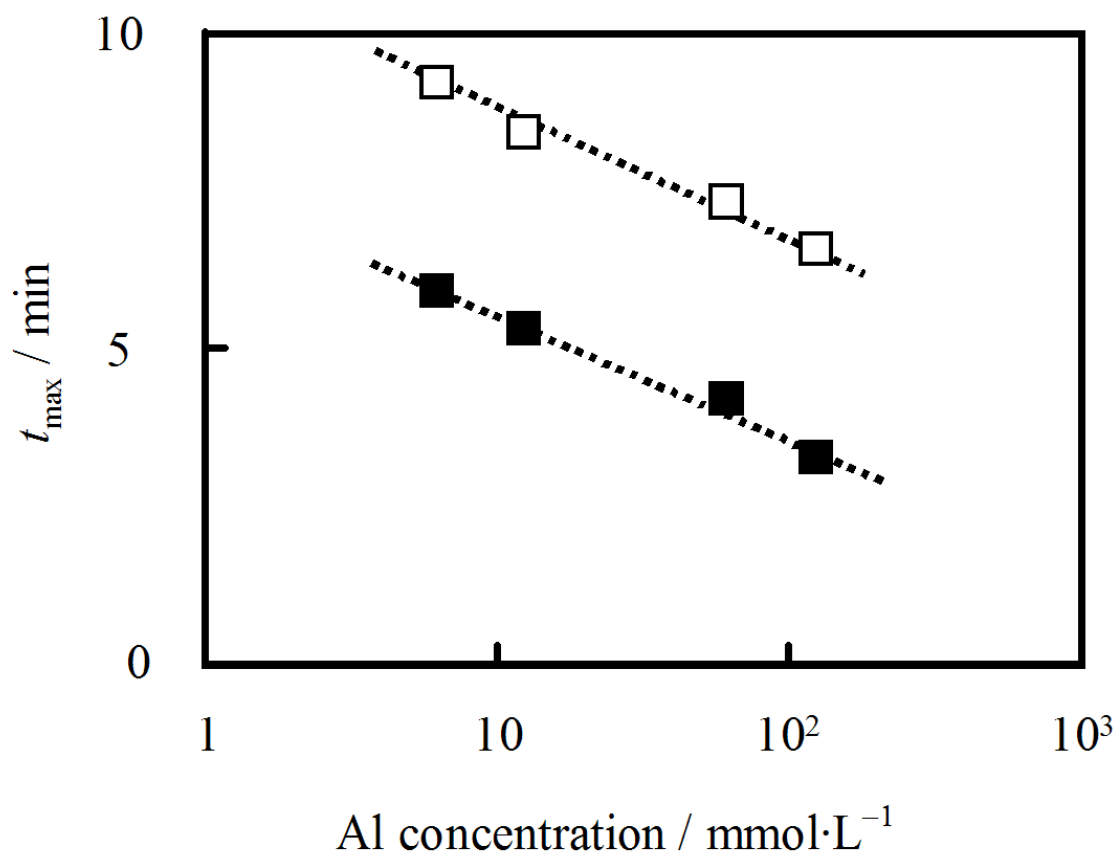


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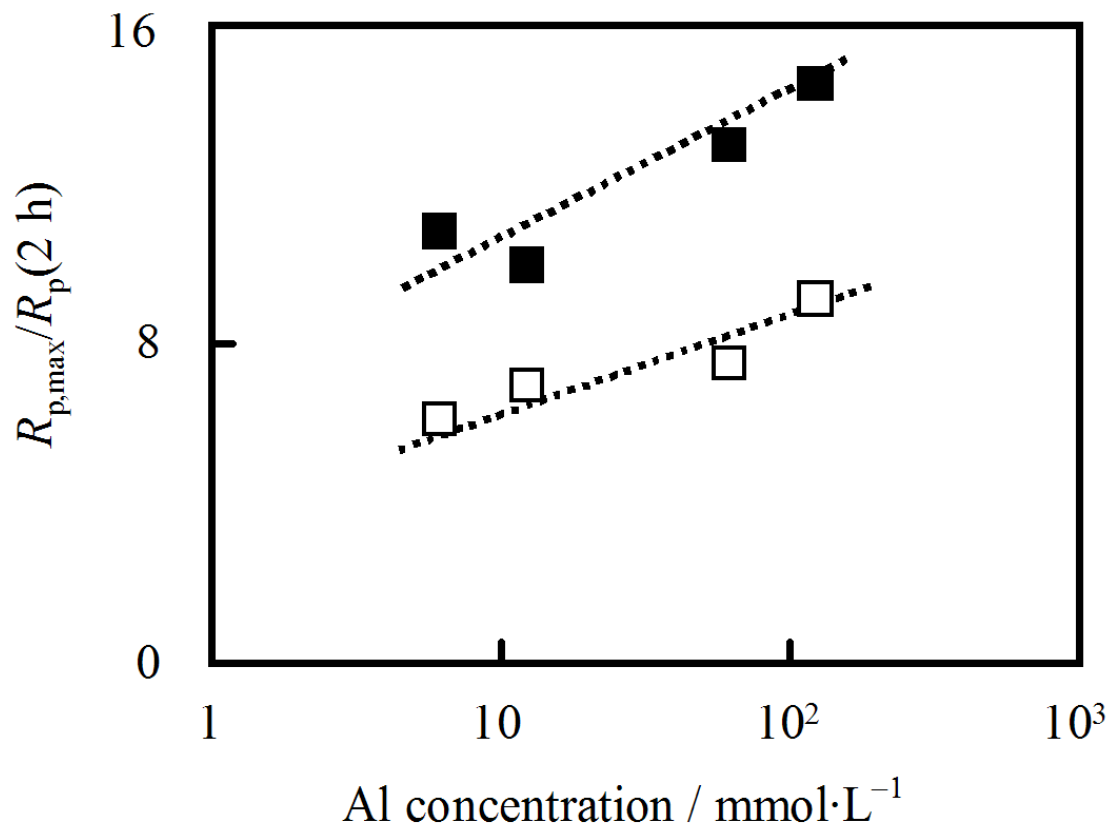


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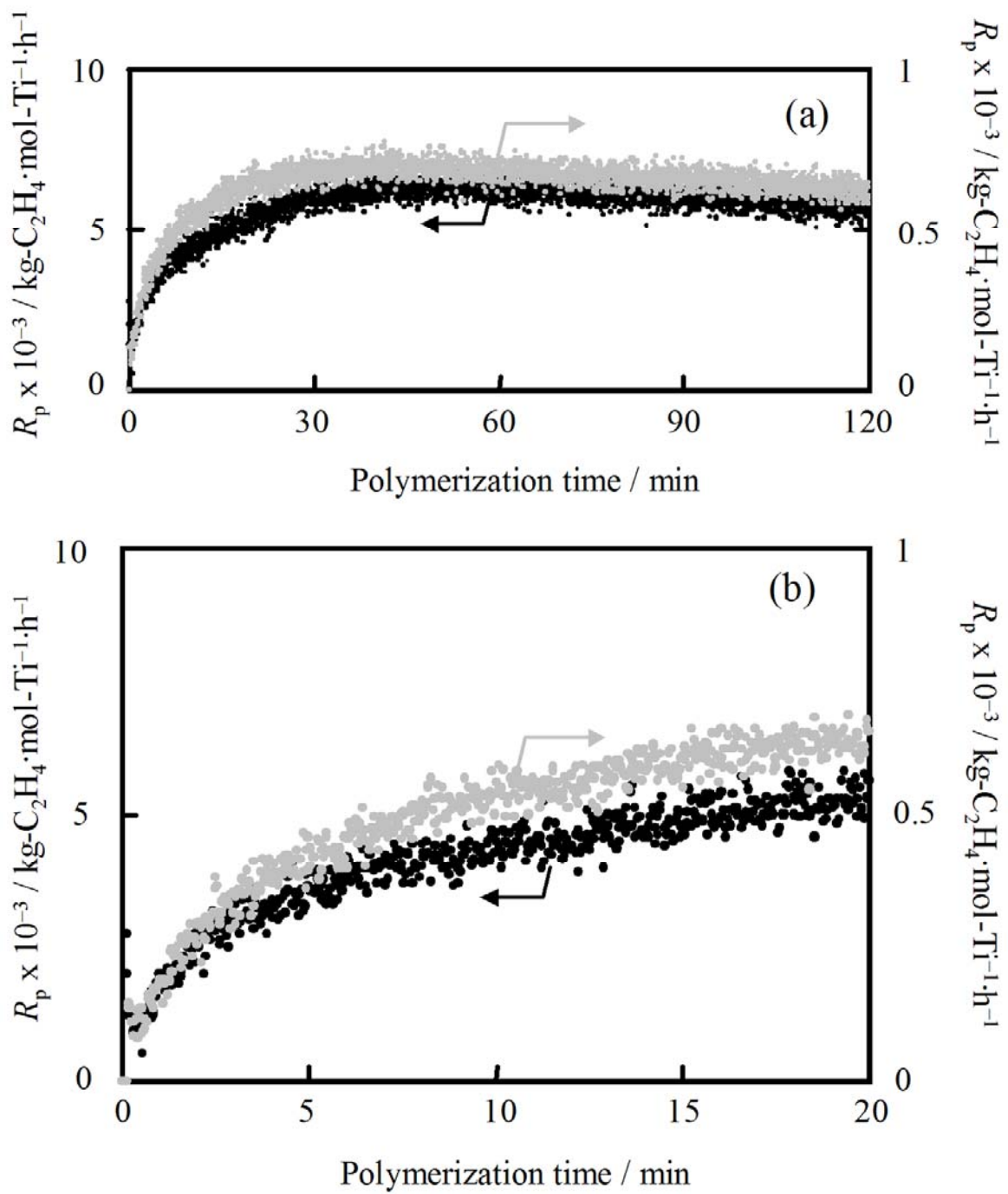


Figure 5. Taniike et al.

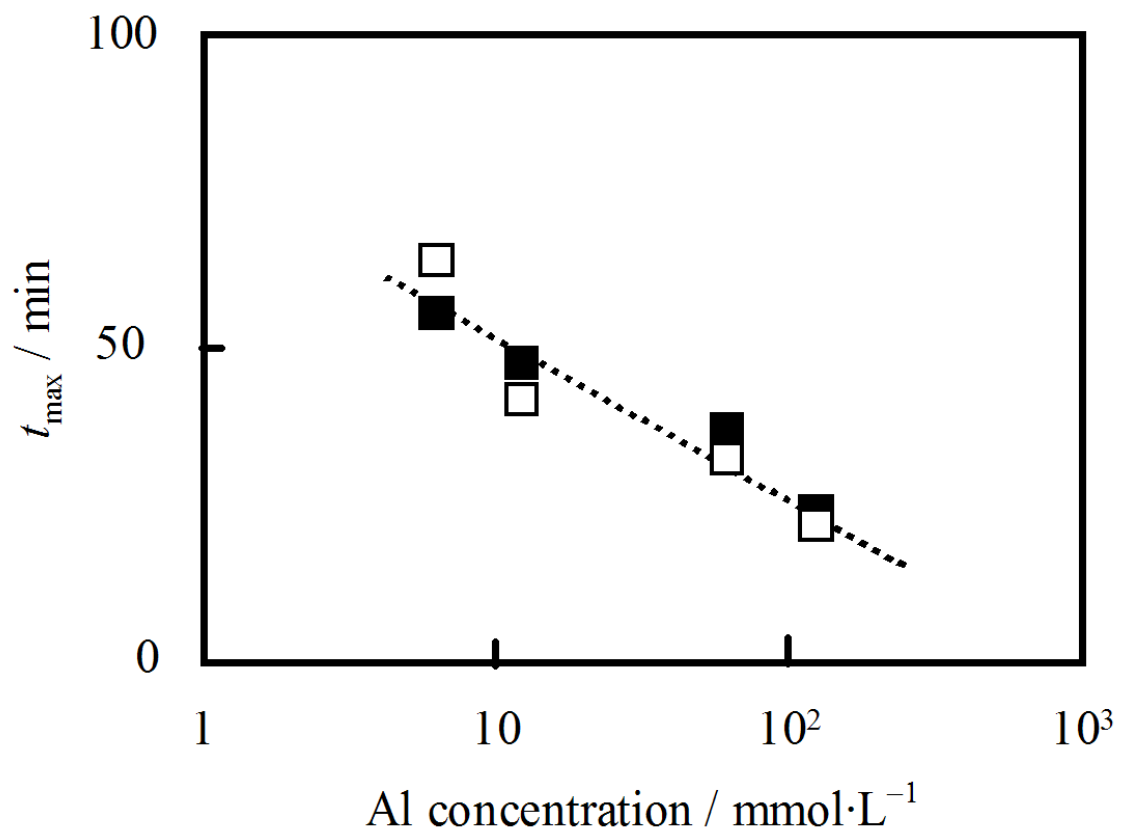


Figure 6. Taniike et al.

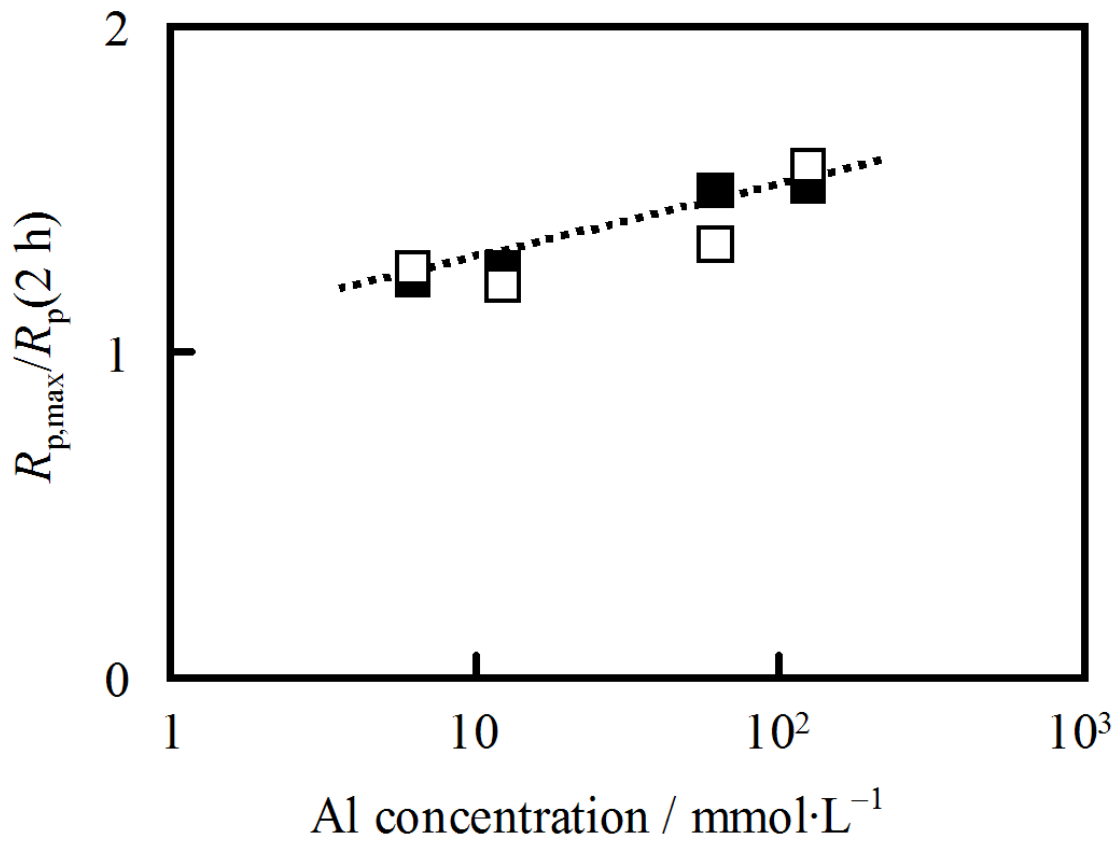


Figure 7. Tanike et al.



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Deactivation behaviors of  $\text{TiCl}_3/\text{MgCl}_2$  model catalysts with molecularly dispersed  $\text{TiCl}_3$  were investigated to clarify the role of the dispersion state of the Ti species in the deactivation of  $\text{MgCl}_2$ -supported Ziegler-Natta catalysts for propylene and ethylene polymerization.

