

Kinetic Study of a Highly Active MgCl_2 -Supported Ziegler–Natta Catalyst in Liquid Pool Propylene Polymerization. II. The Influence of Alkyl Aluminum and Alkoxysilane on Catalyst Activation and Deactivation

FUMIHIKO SHIMIZU,¹ JOCHEM T. M. PATER,² WIM P. M. VAN SWAAIJ,² GÜNTER WEICKERT²

¹ Science and Technology Research Center, Mitsubishi Chemical Corporation, 1000, Kamoshida-cho, Aoba-ku, Yokohama, 227-8502, Japan

² Process Technology Institute Twente, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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ABSTRACT: The influence of alkyl aluminum and alkoxysilane on the kinetics in liquid pool propylene batch polymerization was investigated with a highly active Ziegler–Natta catalyst system that consisted of $\text{MgCl}_2/\text{TiCl}_4/\text{diester-alkoxysilane}/\text{AlR}_3$. In this study, diethyl phthalate and *t*-BuEtSi(OMe)₂ were used as a diester and an alkoxysilane, respectively. The catalyst activity depended on the concentration of the alkyl aluminum when it came into contact with the catalyst. In addition, alkoxysilane as an external donor had a role in activating the catalyst. With respect to activity decay, the overreduction of Ti did not seem to be the cause. Instead, the decay rate decreased with an increasing alkoxysilane/catalyst ratio. This implied that activity decay was caused by the formation of dormant sites after 2,1-misinsertion of propylene. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2669–2679, 2002

Key words: MgCl_2 -supported Ziegler–Natta catalysts; activation; activity decay; dormant site; alkoxysilane

INTRODUCTION

The behavior of highly active MgCl_2 -supported Ziegler–Natta catalysts has been widely studied because of their commercial importance.¹ However, there are many unsolved problems even now regarding the mechanism of MgCl_2 -supported Ziegler–Natta catalysts. One reason is that spectroscopic methods are almost useless for MgCl_2 -supported Ziegler–Natta catalysts, especially in the working state. Another reason is the complex-

ity of Ziegler–Natta catalysts. For example, the catalyst system basically consists of three components: (1) a solid catalyst component, (2) an alkyl aluminum compound as a cocatalyst, and (3) an external donor (ED) as a stereoregularity-controlling reagent. In the working state, they react with one another to form complex species. Therefore, it is difficult to clarify the mechanism and roles of each component. Furthermore, the heterogeneity of the active sites makes the situation more complicated.

MgCl_2 -supported Ziegler–Natta catalysts for propylene polymerization can be classified into three types according to their internal donors:¹ (1) monoester systems, (2), diester systems, and (3) diether systems. Interestingly, the number of

Correspondence to: F. Shimizu (qff01604@nifty.com).

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Table I Suitable Combinations of Internal and External Donors

System	Internal Donor	External Donor	Example
1	Monoester	Monoester	Ethyl benzoate + ethyl benzoate
2	Diester	Alkoxysilane	Di- <i>n</i> -butyl phthalate + PES
3	1,3-Diether	None	2,2- <i>i</i> -Pr ₂ -1,3-Dimethoxypropane

suitable combinations of internal donors and EDs is limited in each system, as shown in Table I.¹ Among these, catalysts of the second type are most widely used in commercial polypropylene (PP) production. Hence, kinetic studies of diester systems would be most important. However, in comparison with monoester systems, diester systems have not been studied sufficiently.

Therefore, we started a kinetics study of propylene polymerization with a highly active MgCl₂-supported Ziegler–Natta catalyst (the MgCl₂/TiCl₄/diester–alkoxysilane/trialkyl aluminum system). Moreover, a calorimetric method for measuring the rate of polymerization (R_p) in a propylene liquid pool was developed at Twente University.²

In this article, the following questions are discussed:

1. What is the role of triethyl aluminum (TEA) and alkoxysilane in the activation and deactivation of the catalyst in liquid propylene polymerization?
2. Is the TEA/Ti ratio, which has been widely used, an important parameter for the kinetic characterization of the catalyst system?
3. Does alkoxysilane act only as a stereoregularity-controlling reagent?

EXPERIMENTAL

Catalyst Preparation

A catalyst of the type MgCl₂/TiCl₄/diethyl phthalate (DEP) was prepared in the following manner. In a 500-mL glass flask, 5.0 g of Mg(OEt)₂ (purchased from Tosoh Corp.) and 1.0 g of DEP (purchased from Tokyo Chemical Industry Co., Ltd.) were treated with a mixture of TiCl₄ (82.9 g; purchased from Toho Titanium Co., Ltd.) and toluene (87.4 mL) at 110°C for 1 h under a nitrogen atmosphere. The solid product was washed three times with 100 mL of toluene by decantation. The

obtained solid product was used as a solid catalyst component, where the Ti content was 2.6 wt %.

Polymerization Procedure

The cocatalyst used was TEA (purchased from Akzo Nobel N.V.). In this study, *t*-BuEtSi(OMe)₂ (purchased from Dow Corning Toray Silicone) was used as an ED.

The experimental setup for liquid pool polymerization consisted of a 5-L jacketed calorimeter, a catalyst injection system, and purification systems for propylene, H₂, and pentane. The details of the setup were described previously.^{2,3} Polymerizations were carried out batchwise under isothermal conditions. During polymerization, the difference between the reactor and jacket temperatures was measured at intervals of 20 s to calculate R_p .

The 5-L calorimeter mentioned previously was initially charged with known amounts of H₂ and 2600 mL of liquid propylene. The H₂ concentration in the gas phase of the reactor was fixed around 3% (v/v). The reactor was then heated, and when the reactor temperature reached 70°C, TEA and the ED were added. Next, a known amount of the solid catalyst component was injected to start the polymerization. During the polymerization, a master–slave PID controller regulated the reactor temperature at 70°C with an accuracy of 0.1 K, except for the initial several minutes. The polymerization was finally terminated by rapid flushing of the unreacted propylene.

Preactivation of the Catalyst

In this study, 11 experiments were carried out to investigate the effect of preactivation by TEA and ED. In runs 1–3, the solid catalyst component was injected without preactivation, whereas in runs 4–11, the solid catalyst component was preactivated in the presence of TEA and the ED before the polymerization began. The preactivation was carried out in the following manner. In a 20-mL

bottle, a known amount of the solid catalyst component and 5 mL of pentane were added at room temperature. Known amounts of TEA and the ED were then added. The amounts of TEA and the ED used in the preactivation are shown in Table II. Afterward, the bottle was shaken for 30 min at 15°C before injection into the reactor.

Isotactic Index

The isotactic index is a measure of the stereoregularity of PP. It was measured in the following manner. One gram of PP powder was precisely weighed in a 300-mL glass flask, and this was followed by the addition of 200 mL of xylene. Through heating, the PP powder was completely dissolved in boiling xylene. The solution was rapidly cooled in a water bath at 25°C, and the precipitate was filtered. From the filtrate, 50 mL of the portion was sampled and dried on a platinum plate. The residue was thoroughly dried *in vacuo*. Finally, the isotactic index was calculated as the weight percentage of the insoluble part.

RESULTS AND DISCUSSION

Kinetics

A typical kinetic curve with a preactivated catalyst is shown in Figure 1. In a Ziegler–Natta catalyst that belongs to a diester system (see Table I), the kinetics of homopolymerization can generally be described with first-order decay.^{1,4,5} It is modeled under the assumptions that (1) R_p is directly proportional to the monomer concentra-

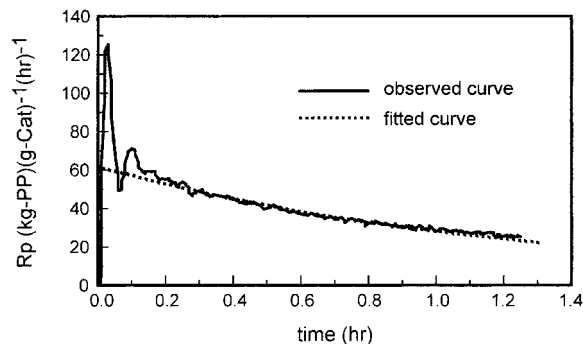


Figure 1 Typical kinetic curve.

tion (C_m) and active site concentration (C^*), (2) C^* decreases in accordance with first-order decay, and (3) there are no C_m and temperature gradients in the growing polymer particles. These assumptions are usually approximately correct in diester systems used for liquid propylene polymerization. Therefore, we can write

$$R_p = k_p C_m C^*$$

$$\frac{dC^*}{dt} = -k_d C^* \quad (1)$$

where k_p is a propagation rate constant and k_d is a decay constant. Note that C_m remains constant in liquid pool polymerization under equilibrium conditions. If we assume isothermal conditions, the next equation, which describes the relationship between time (t) and R_p , can be obtained from eq. (1):

$$R_p = R_{p,0} \exp(-k_d t) \quad (2)$$

where $R_{p,0}$ is the initial polymerization rate. Figure 1 shows that the observed kinetic curve is well fitted by eq. (2), with the exception of the first few minutes of the reaction. The reason for this is that it is rather difficult to precisely control the jacket temperature, and the quasi-steady-state assumption regarding heat transfer is not valid immediately after catalyst injection. Note that in such calorimetric measurements, small temperature deviations in the jacket can lead to large apparent oscillations in R_p at the beginning of polymerization. Other kinetics in this article are similarly fitted by eq. (2), that is, first-order decay kinetics.

Table II Preactivation Conditions

Run	Preactivation	Catalyst (mg)	TEA (mg)	ED ^a (mg)
1	No	—	—	—
2	No	—	—	—
3	No	—	—	—
4	Yes	4.0	1.65	1.11
5	Yes	7.7	2.50	1.70
6	Yes	6.2	2.50	1.70
7	Yes	5.9	2.50	1.70
8	Yes	10.3	2.50	1.70
9	Yes	9.6	2.50	1.70
10	Yes	9.6	1.70	1.10
11	Yes	5.6	1.70	1.10

^a As the ED, *t*-BuEtSi(OMe)₂ was used.

Table III Results of Polymerization

Run	Preactivation	Catalyst (mg)	TEA ^a (mg)	ED ^a (mg)	$R_{p,0}$ [(kg of PP) (g of Catalyst) ⁻¹ h ⁻¹]	k_d h ⁻¹
1	No	6.0	360.6	18.8	12.1	0.342
2	No	12.7	369.8	17.4	13.4	0.316
3	No	11.7	373.3	17.8	11.2	0.194
4	Yes	4.0	170.0	0.0	55.5	1.236
5	Yes	7.7	116.6	4.4	72.8	1.334
6	Yes	6.2	50.4	2.2	70.5	1.116
7	Yes	5.9	245.4	10.4	57.1	0.499
8	Yes	10.3	246.7	10.4	57.0	0.741
9	Yes	9.6	239.1	10.4	67.3	0.865
10	Yes	9.6	240.0	10.4	58.9	0.931
11	Yes	5.6	171.3	7.4	62.3	0.780

^a The amounts of TEA and the ED which were directly added in the reactor are shown.

Role of Alkyl Aluminum and an Alkoxysilane: Catalyst Activation

As shown previously, the model contains two parameters: $R_{p,0}$ and k_d . Therefore, we take notice of these two parameters. The results of the experiments in this study are summarized in Table III, which contains $R_{p,0}$, k_d , and the polymerization conditions.

Table III clearly shows that $R_{p,0}$ is quite low without preactivation, whereas a much higher $R_{p,0}$ value is observed with preactivation. In Figure 2, a typical example is shown for a comparison of the differences between these two cases. Figure 2 also shows that it takes a relatively long time for R_p to reach its maximum without preactivation. However, R_p reaches the maximum almost instantaneously with preactivation. From these experimental facts, we can conclude that the preactivation of the catalyst with TEA and the ED is effective for activating the catalyst. Therefore,

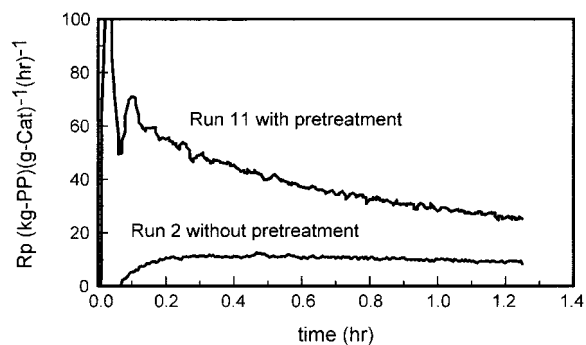


Figure 2 Comparison of the kinetics with and without preactivation.

what are the roles of TEA and the ED in the activation of the catalyst? Do the preactivation conditions have any influence on the kinetics?

In diester systems, the following reactions occur when the solid catalyst component comes into contact with TEA and an ED:

1. Reduction of the tetravalent Ti ion (Ti^{4+}) into the trivalent Ti ion (Ti^{3+}).⁶⁻¹²
2. Removal of the diester from the solid catalyst component. An ED such as alkoxysilane forms a surface complex with Mg ion on the surface of the solid catalyst component.^{1,13,14}

Such reactions can be related to the mechanism of catalyst activation. In fact, it is possible to interpret our experimental data from this point of view.

First, let us discuss the role of TEA. It is well known that trivalent Ti ions (Ti^{3+}) are the actual active species for propylene polymerization.⁶⁻¹² Because Ti ions exist in the tetravalent state (Ti^{4+}) in their original form, it is necessary to reduce Ti^{4+} into Ti^{3+} with a suitable reducing reagent such as TEA to activate the catalyst.

Therefore, we investigated the relationship between $R_{p,0}$ and various parameters concerning TEA, such as the TEA/Ti molar ratio and TEA concentration. Interestingly, only the initial TEA concentration, that is, the TEA concentration when the solid catalyst component comes into contact with TEA for the first time, shows a clear tendency against $R_{p,0}$. The importance of the TEA concentration for catalyst activation was also

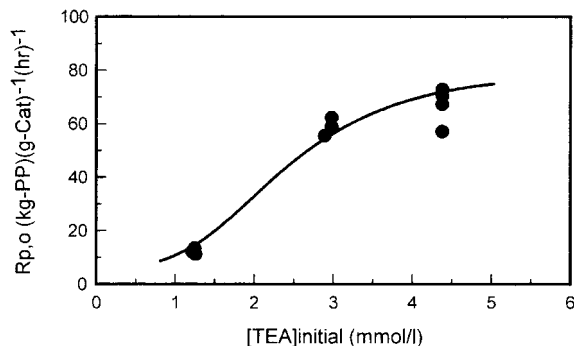


Figure 3 Relationship between the initial TEA concentration and $R_{p,0}$.

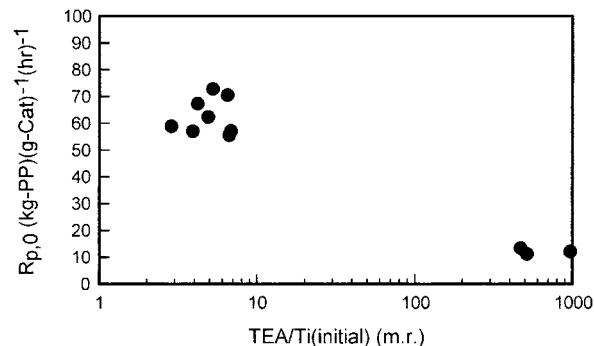


Figure 4 Relationship between the initial TEA/Ti molar ratio and $R_{p,0}$.

pointed out by Spitz et al.¹⁵ Note that the initial TEA concentration without preactivation is low because TEA is dissolved in a large amount (2600 mL) of liquid propylene. However, the initial TEA concentration with preactivation is high because the amount of the solvent is very small (see the Experimental section).

Figure 3 shows the relationship between the initial TEA concentration and $R_{p,0}$. It is clear that a higher initial TEA concentration gives a higher $R_{p,0}$ value. Conversely, when the initial TEA concentration is low, as in runs 1–3, $R_{p,0}$ is quite low. In addition to such low $R_{p,0}$ values, it takes a relatively long time for R_p to reach the maximum, as mentioned previously. It can be interpreted that catalyst activation is TEA-concentration-dependent. Consequently, after the catalyst is injected into the reactor, potential active sites still remain on the surface of the solid catalyst component, and they will be activated slowly with TEA in the reactor. The observed induction time in runs 1–3 is probably caused by such slow activation. However, when the initial TEA concentration is high, such as in runs 4–11, a much higher $R_{p,0}$ value is observed, and R_p reaches the maximum immediately after the catalyst injection. It can be interpreted that the catalyst is activated to a sufficient extent during the preactivation because of a high TEA concentration. Therefore, the catalyst shows immediate high activity when it is injected into the reactor.

One may think that $R_{p,0}$ should be related to the initial TEA/Ti ratio because TEA/Ti is a traditional parameter that has long been used. Figure 4 shows the relationship between the initial TEA/Ti ratio and $R_{p,0}$. Apparently, a high initial TEA/Ti ratio seems to give low $R_{p,0}$, although this might be contrary to one's expectation. As an expedient explanation, it may be possible to say

that a high initial TEA/Ti ratio causes an overreduction of Ti, resulting in low $R_{p,0}$. However, the experimental facts deny this explanation. Figure 5 shows the kinetics in run 12, for which the influences of TEA and an alkoxysilane as an ED on the kinetics were investigated. However, we focus our attention on the influence of TEA at first. The initial TEA/Ti molar ratio is 276 (shown later in Table V), which is high enough to give low $R_{p,0}$ if we assume an imaginary relationship between the initial TEA/Ti ratio and $R_{p,0}$. The $R_{p,0}$ value of this run is low indeed, as shown in Figure 5. However, the catalyst activity increases when additional TEA is injected at $t = 0.40$ h. It is quite unlikely that initially overreduced Ti is activated by TEA again because TEA is a reducing reagent. Therefore, we can say that the assumed apparent relationship shown in Figure 4 is a misleading one. In other words, the initial TEA/Ti ratio is not a good parameter as an index of $R_{p,0}$.

In conclusion, the difference in $R_{p,0}$ with and without preactivation is attributed to the difference in the initial TEA concentration, and the

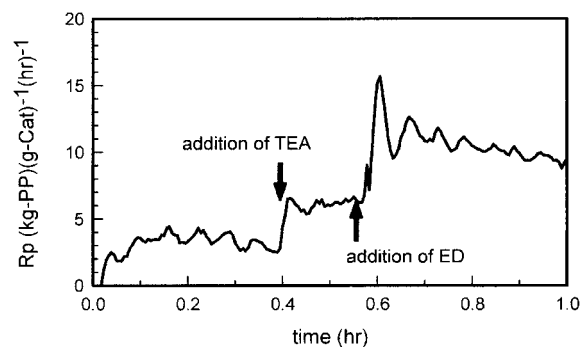


Figure 5 Influence of TEA and the ED on the kinetics.

Table IV Distribution of Titanium Oxidation State

Treatment	Ti ²⁺ (%)	Ti ³⁺ (%)	Ti ⁴⁺ (%)
TEA	19.3	73.7	7.0
TEA/PES	33.4	38.5	28.1

From Chien and Hu.¹²

catalyst requires a higher TEA concentration for activation.

Therefore, why is a high initial TEA concentration required for catalyst activation? Chien and Hu¹² measured the distribution of the Ti oxidation state in a diester/alkoxysilane catalyst system in which the internal donor was di-*n*-butyl phthalate and the ED was PhSi(OEt)₃ (PES). Some of their results are shown in Table IV. It is noteworthy that 28.1% of Ti remains unreduced in the presence of PES. This result shows that a more effective way is needed to reduce such remaining tetravalent Ti in the diester/alkoxysilane catalyst system. Increasing the TEA concentration can be effective for reducing tetravalent Ti because a chemical reaction is generally accelerated with an increase in the concentration of the reactants. Another effect of increasing the TEA concentration would be the enhanced removal of the internal donor, but this will be discussed later.

Next, we investigated the role of the ED. Sacchi et al.¹³ investigated a diester/alkoxysilane catalyst system in which the internal donor was diisobutyl phthalate and the ED was PES. They found that the productivity of isotactic PP increased with an increasing amount of ED absorbed on the solid catalyst component. Similarly, Albizzati et al.¹ proposed that the initial activity of the catalyst increased with an increasing amount of alkoxysilane incorporated into the solid catalyst component. Spitz et al.¹⁶ reported

that R_p increased with an increasing ED/TEA molar ratio between 0 and 0.05. All these results imply that an alkoxysilane as an ED can contribute to catalyst activation.

Let us go back to Figure 5 again. This time, we focus our attention on the influence of alkoxysilane as an ED on the kinetics. The polymerization conditions were basically the same as in run 1; that is, the catalyst was injected into the reactor without preactivation (see Table V). Because of the low initial TEA concentration, the polymerization began with a very low value of $R_{p,0}$, as already explained. In other words, a large portion of potential active sites remained inactive according to our interpretation. At $t = 0.56$ h, another portion of ED was added instead of TEA. Again, an increase in R_p was observed. This result shows that alkoxysilane as well as TEA is actually involved in the activation of the catalyst, as reported by Spitz and coworkers.^{15,16} Figure 5 also shows that the response of ED addition is rather fast. This means that the coordination equilibrium of alkoxysilane is rapid between liquid propylene and the surface of the solid catalyst component even at low concentrations, as was suggested by Spitz et al.¹⁵

The mechanism of activation by alkoxysilane was explained by Spitz et al.¹⁵ Alkoxysilane as an ED converts a fluctuating site, which produces less isotactic PP, into a highly isotactic site.^{1,17} In general, the activity is higher at highly isotactic sites than at less isotactic sites because the propagation constant is higher at highly isotactic sites.^{1,18} Therefore, the activity increases with the addition of alkoxysilane up to the point at which the silane concentration becomes too high to inhibit active sites.

Let us discuss the role of TEA once more. We have mentioned that the initial TEA concentration is related to the efficiency of the reduction of tetravalent Ti ion. In addition, the initial TEA concentration affects the efficiency of the removal

Table V Polymerization Conditions in Run 12^a

Time (h)	Event	Catalyst (mg)	TEA (mg)	ED (mg)	TEA/Ti (Molar Ratio)
0.00	Initial conditions		370.0	19.6	
0.40	Injection of the catalyst	21.6			276
0.40	Addition of TEA		374.8		556
0.56	Addition of ED			19.5	

^a In this run, polymerization was carried out without preactivation.

Table VI Comparison of $[\text{TEA}]_{\text{ini}}$ and $[\text{ED}]_{\text{ini}}$ ^a

Run	$[\text{TEA}]_{\text{ini}}$ (mmol/L)	$[\text{ED}]_{\text{ini}}$ (mmol/L)	$[\text{TEA}]_{\text{ini}}[\text{ED}]_{\text{ini}}$ (mmol/L) ²	$R_{p,0}$ [(kg of PP) (g of Catalyst) ⁻¹ h ⁻¹]
1	1.22	0.04	0.05	12.1
2	1.24	0.04	0.05	13.4
3	1.26	0.04	0.05	11.2
4	2.89	1.26	3.64	55.5
5	4.38	1.93	8.45	72.8
6	4.38	1.93	8.45	70.5
7	4.38	1.93	8.45	57.1
8	4.38	1.93	8.45	57.0
9	4.38	1.93	8.45	67.3
10	2.98	1.25	3.73	58.9
11	2.98	1.25	3.73	62.3

^a In Runs 4–11, $[\text{TEA}]_{\text{ini}}$ and $[\text{ED}]_{\text{ini}}$ are the concentrations at preactivation.

of the internal donor. In a diester catalyst system, a diester as an internal donor can be removed relatively easily, probably via complex formation with TEA. Therefore, increasing the initial TEA concentration would lead to the enhanced removal of the internal donor, which is advantageous for the incorporation of alkoxy silane as an ED. Because increasing the amount of the ED absorbed on the solid catalyst component leads to increasing catalyst activity, which was shown not only by Albizzati, Sacchi, and Spitz but also by our experiments, increasing the initial TEA concentration would be indirectly involved with catalyst activation through internal-donor and ED exchange.

In conclusion, the preactivation of the solid catalyst component with TEA and an ED is an effective method for obtaining high activity. In this preactivation, TEA and the ED come into contact with the solid catalyst component at relatively high concentrations, which leads to high activity because the tetravalent Ti ion is reduced effectively and the exchange of the internal donor and ED occurs smoothly.

Reconsideration: Catalyst Activation

In the previous discussion, the roles of TEA and the ED were separated. However, one might think that a complex of TEA and the ED may be an actual species for catalyst activation because it is well known that TEA and alkoxy silane readily form a complex^{1,15,19,20} and we used both in the preactivation (see the Experimental section). In addition, it could be assumed that a high ED concentration might be another necessary condition for catalyst activation.

Table VI shows a comparison of $[\text{TEA}]_{\text{ini}}$ and $[\text{ED}]_{\text{ini}}$, where $[\text{TEA}]_{\text{ini}}$ and $[\text{ED}]_{\text{ini}}$ are the concentrations of TEA and the ED when the solid catalyst component initially contacted them. In fact, only a low activity was obtained when $[\text{ED}]_{\text{ini}}$ was low, at least in Table VI. Also, the activity was low when the product of $[\text{TEA}]_{\text{ini}}[\text{ED}]_{\text{ini}}$ was small, which may imply that complexation between TEA and the ED is involved with catalyst activation.

To investigate such possibilities, we carried out an additional experiment (run 13) in the following manner:

1. The solid catalyst component (11.6 mg) was treated only with TEA at a relatively high concentration ($[\text{TEA}]_{\text{ini}} = 13.1$ mmol/L).
2. Liquid propylene (2600 mL) was introduced and heated to 70°C. The H₂ concentration in the gas phase of the reactor was fixed at 3% (v/v).
3. TEA (210 mg) was added into the reactor.
4. The treated solid catalyst component was injected into the reactor.
5. Immediately after catalyst injection, the ED (10.4 mg) was added into the reactor ($[\text{ED}]_{\text{ini}} = 0.02$ mmol/L).
6. The activity was evaluated by the polymer yield per unit amount of catalyst per hour, that is, the polymerization velocity (V_p), at 25 min.

Note that this condition is similar to that of runs 8–10, except that the solid catalyst component was treated only with TEA. If $[\text{ED}]_{\text{ini}}$ is important for catalyst activation, the activity un-

Table VII Result of Run 13

Run	$[\text{TEA}]_{\text{ini}}[\text{ED}]_{\text{ini}}$ (mmol/L) ²	V_p ($t = 25$ min) [(kg of PP) (g of Catalyst) ⁻¹ (h) ⁻¹]
1	0.05	11.3
4	3.64	43.3
8	8.45	49.0
13	0.02	59.6

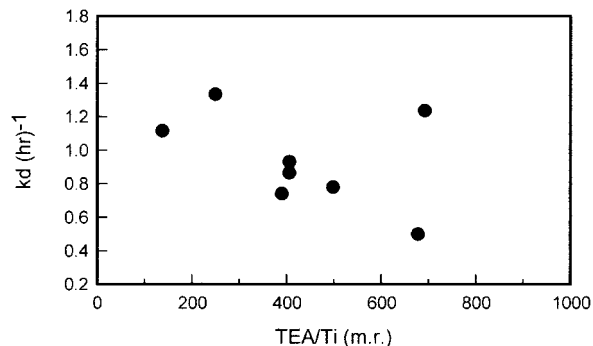
der this condition should be significantly lower because $[\text{ED}]_{\text{ini}}$ was only 0.02 mmol/L, which was much lower than that of runs 1–3. Furthermore, if complexation is important for catalyst activation, the activity also should be low because the product of $[\text{TEA}]_{\text{ini}}[\text{ED}]_{\text{ini}}$ in the reactor was only 0.02 (mmol/L)², which was also lower than that of runs 1–3.

Table VII shows the results of this additional experiment (run 13). It is clear that a high activity was obtained even at this condition; that is, a high activity was obtained even though $[\text{ED}]_{\text{ini}}$ was low and $[\text{TEA}]_{\text{ini}}[\text{ED}]_{\text{ini}}$ was small. These results allow us to say that neither a high ED concentration nor a complex formation of TEA and ED is essential for catalyst activation.

Role of Alkyl Aluminum and an Alkoxysilane: Activity Decay

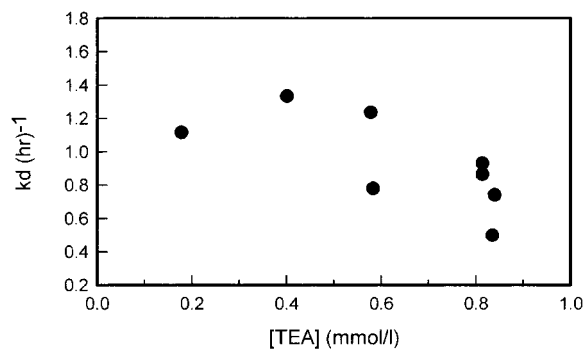
To discuss activity decay, we have selected the data in runs 4–11 because the kinetics in these runs followed first-order decay, as shown in Figure 1. In these runs, the catalyst was preactivated before polymerization began. Therefore, catalyst activation was no longer important after polymerization started. In contrast to these runs, the kinetics in runs 1–3 were more complicated, probably because the catalysts without preactivation were not fully activated initially, and catalyst activation still proceeded even after polymerization began.

The reason for activity decay is not completely clear. Some researchers have already proven that activity decay is not caused by mass-transfer limitations of propylene through PP shells that grow around the catalyst particles as polymerization proceeds.^{1,21–24} Because k_p values do not change significantly during the course of polymerization,^{25,26} it would be reasonable to say that the activity decay is caused by a decrease in the number of active sites. If so, why does the number of active sites decrease during polymerization?

**Figure 6** Relationship between the TEA/Ti molar ratio and k_d .

One hypothesis is that it occurs via overreduction of Ti^{3+} into Ti^{2+} by TEA.^{1,10,24} Because TEA is a powerful reducing reagent and Ti^{2+} is inactive to propylene polymerization,^{6,8,11} this hypothesis seems to be reasonable. If this is correct, the molar ratio of TEA to Ti in the reactor or the TEA concentration in the reactor should have a strong effect on the rate of activity decay. Figures 6 and 7 show the relationship between the observed k_d values and the TEA/Ti molar ratio or TEA concentration, respectively. Obviously, there is no clear tendency between k_d and TEA/Ti or k_d and the TEA concentration. A weak tendency could be assumed between k_d and the TEA concentration in Figure 7. However, Figure 7 apparently shows that a higher TEA concentration gives a smaller value of k_d , which is a completely different from what would follow from the overreduction point of view; that is, this apparent trend lacks consistency. Therefore, these results allow us to say that the hypothesis of overreduction as the cause of activity decay is questionable.

Another hypothesis that reasonably explains the decrease in the number of active sites is the

**Figure 7** Relationship between the TEA concentration and k_d .

concept of dormant sites. According to Corradini et al.,²⁷ it has long been suspected that occasional 2,1-secondary inserted monomer units can slow down chain propagation. This was experimentally confirmed by Busico et al.²⁸ and Chadwick et al.²⁹ with ¹³C-NMR analyses of the chain end groups of PP formed via H₂-induced chain transfer. Another mechanism related to dormant sites was proposed by Spitz et al.³⁰ They proposed that the π -allyl structure formed via β -H elimination from a coordinated monomer on a Ti ion could be a dormant site. The formation of π -allyl species was confirmed by Guyot et al.³¹ with propylene deuteration experiments. They also suggested that π -allyl formation after 2,1-insertion is a preferred path, which means 2,1-insertion can slow down R_p . This suggests that, regardless of the actual structure of the dormant site, 2,1-insertion leads to activity decay. This hypothesis is called *dormant site theory* in the following.

If the dormant site theory is correct, it is suspected that alkoxysilane as an ED could be involved with activity decay. Because 2,1-insertion is a kind of misinsertion, it should occur more often at aspecific sites than at isospecific sites. In fact, Corradini et al.²⁷ estimated the fraction of the dormant sites in the MgCl₂/bis(2-ethylhexyl)-phthalate (BEHP)/TiCl₄-PES/TEA system and the MgCl₂/TiCl₄-TEA system. Needless to say, the latter shows very poor isotacticity due to the lack of an internal donor and an ED. The estimated dormant sites were 20% in the former system and 50% in the latter system. Furthermore, Kojoh et al.³² investigated the type of chain transfer without H₂ in the MgCl₂/TiCl₄/dioctyl phthalate (DOP)-diphenyldimethoxysilane (DPDMS)/TEA system. They reported that 2,1-insertion was easily observed without DPDMS but not observed with DPDMS. Because the stereoregularity is sig-

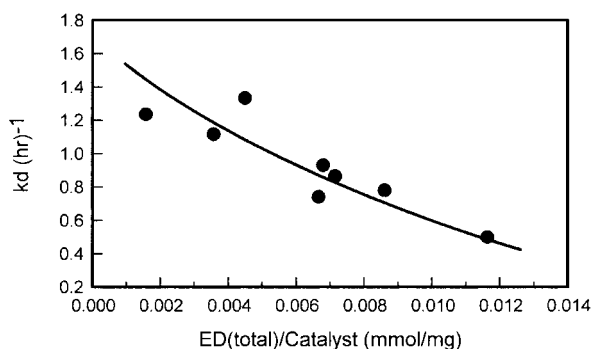


Figure 8 Relationship between the ED (total)/catalyst ratio and k_d .

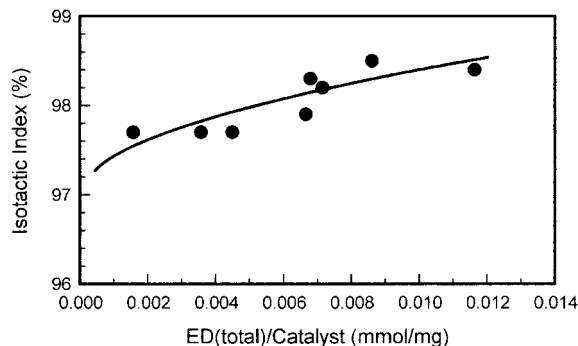


Figure 9 Relationship between the ED (total)/catalyst ratio and the isotactic index.

nificantly poorer without DPDMS, this result is consistent with the idea that 2,1-insertion occurs more often at aspecific sites than at isospecific sites. In summary, it is expected that improving the stereoregularity of the catalyst should lead to decreases in the dormant sites, which should result in the slowing down of activity decay.

Figure 8 shows the relationship between k_d and the ED (total)/catalyst ratio, where ED (total) is the sum of the amount of ED in the preactivation and polymerization. Because an ED molecule forms a surface complex with Mg²⁺ ions, not with Ti ions,^{1,33,34} it would be more reasonable to use the ED/catalyst ratio rather than the ED/Ti ratio. Figure 8 clearly shows that k_d decreases with an increasing ED (total)/catalyst ratio. At the same time, we measured the isotactic index of PP (see Fig. 9). It is obvious that the isotactic index of PP increases with an increasing ED (total)/catalyst ratio. These experimental facts are fully consistent with our expectation that improving the stereoregularity of the catalyst leads to the slowing down of activity decay.

Interestingly, there is no clear tendency between k_d and the ED (preactivation)/catalyst ratio, where ED (preactivation) is the amount of ED in the preactivation (see Fig. 10). This can be explained by rapid coordination of alkoxysilane between liquid propylene and the surface of the catalyst.¹⁵ Because of such fast equilibrium, not only the ED that is added at the preactivation but also the ED that is added into the reactor can form a surface complex rapidly to work as a stereoregularity-controlling reagent. Therefore, the factor that controls k_d is not the ED (preactivation)/catalyst ratio but the ED (total)/catalyst ratio. Such rapid equilibrium is supported by the fact that the response of ED addition on catalyst activity was very fast (see Fig. 5).

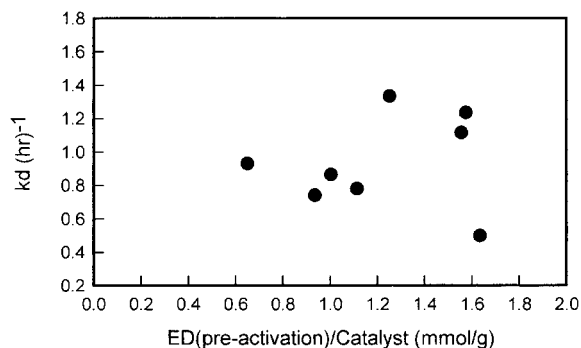


Figure 10 Relationship between the ED (preactivation)/catalyst ratio and k_d .

CONCLUSIONS

The influence of alkyl aluminum and alkoxy silane on the activation and deactivation of Ziegler–Natta catalysts was studied with the $\text{MgCl}_2/\text{TiCl}_4/\text{diester-alkoxy silane}/\text{AlR}_3$ system. In the activation of the catalyst, both alkyl aluminum and alkoxy silane are involved. One of the roles of alkyl aluminum in the activation is the reduction of Ti^{4+} into Ti^{3+} , which is an active form for propylene polymerization. Another role of alkyl aluminum is the removal of the diester from the surface of the catalyst, resulting in enhanced coordination of alkoxy silane as an ED, which leads to the formation of highly isotactic and highly active sites. Therefore, a high TEA concentration is effective for activating the catalyst. The role of alkoxy silane in the activation is the transformation of less isotactic sites into highly isotactic sites. In activity decay during polymerization, the influence of alkyl aluminum cannot be clearly observed. However, activity decay slows down with an increasing ratio of the total amount of alkoxy silane to the amount of catalyst. The role of alkoxy silane is basically improving the stereoregularity of the active sites to decrease 2,1-insertion. With the assumption that activity decay occurs via the formation of dormant sites, which are easily formed after 2,1-insertion, we can reasonably explain the effect of alkoxy silane on activity decay.

NOMENCLATURE

C^*	active site concentration [(g of catalyst) ⁻¹]
C_m	monomer concentration (mol/L)
k_d	decay constant [(h) ⁻¹]

k_p	propagation rate constant [(kg of PP)(L)(h) ⁻¹ (mol) ⁻¹]
R_p	rate of polymerization [(kg of PP)(g of catalyst) ⁻¹ (h) ⁻¹]
$R_{p,0}$	initial rate of polymerization [(kg of PP)(g of catalyst) ⁻¹ (h) ⁻¹]
t	time (h)
V_p	polymerization velocity [(kg of PP)(g of catalyst) ⁻¹ (h) ⁻¹]

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