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KINETIC STUDY FOR THE DECAY RATE OF ETHYLENE POLYMERIZATION CATALYZED OVER SILICA SUPPORTED $TiCl_4/MgCl_2$ CATALYSTS

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Abstract—The kinetics for decay rate of ethylene polymerization catalyzed with $TiCl_4/MgCl_2/SiO_2$ has been investigated in the range of temperatures between 40 and 90°C and in the range of ethylene pressures between 4 and 12.4 atm. The decay of polymerization rate was fitted well by the type of first order decay. The decay rate constant caused by monomer could be expressed by $k_d' = C \cdot [M]^{-1/2}$. Some plausible speculations have been proposed on the deactivation mechanism caused by monomer. The activation energy for the deactivation reaction is 9.8 kcal/mole.

INTRODUCTION

The classical $TiCl_3$ type Ziegler-Natta catalysts have relatively constant rate for long periods of polymerization. This constant rate can be interpreted two ways. One is that the life of active sites are long. The other is that there is a decay of active sites, which are balanced by the creation of new ones when $TiCl_3$ crystals are fragmented during polymerization. Gianini [1] and Keii et al. [2] reported that one of the characteristic features of all $MgCl_2$ supported high activity catalyst systems is to exhibit a rapid decay at the early stage of polymerization. It has been established that this decrease in the rate of polymerization is not associated with the diffusion of monomer through the layer of polymer growing with the progress of the polymerization. It is now more generally accepted that the decrease in polymerization rate is associated either with a rearrangement of some highly active initial site of the catalyst or with a decrease in the number of active centers during the polymerization [1,2]. Silica has been used in the UNIPOL PE process as an useful support in order to provide the opportunity to expose and isolate the maximum amount of catalytically active transition metal compound disclosed in the patent by Wagner et al. [3]. Kim et al. [4] and Kim and Woo [5] have previously observed the silica supported catalyst prepared by the chemical anchoring of $TiCl_4$ to the surface assisted in stabilizing exposed and isolated transition metal centers and controlling the morphology of polymer.

The present paper reports on the decay behavior of ethylene polymerization by highly active silica supported catalyst, which is useful to simulate the polymerization rate profile for the computer control of polymerization reactor.

EXPERIMENTAL

1. Materials

Polymerization grade of ethylene (Yukong Ltd., Korea), nitrogen and hydrogen of extra pure grade were further purified with the columns of Fisher RIDOX catalyst and molecular sieve USA) was used without further purification.

n-Hexane of extra pure grade (Duksan Ltd., Korea) was dried by refluxing over sodium metal in a nitrogen atmosphere. Analytic grade of tetrahydrofuran (J.T. Baker Chem. Co., USA) was purified by refluxing with $LiAlH_4$ for several hours.

Titanium tetrachloride, triethylaluminum, and anhydrous magnesium chloride (Aldrich, USA) were used without further purification. Silica gel (#14-7420) was obtained from Strem Chem. Inc.

2. Polymerization

Silica supported $TiCl_4/THF/MgCl_2$ catalyst was prepared according to the procedure previously described [4]. Slurry polymerization was carried out in all

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autoclave under constant pressure of ethylene [4].

Polymerization rate was determined at every 0.01 sec from the rate of ethylene consumption, measured by a hot-wire flowmeter (model 5850D from Brooks Instrument Div.) with a recorder and a personal computer directly connected to the flowmeter through a A/D converter. Polymer yield estimated from the consumption rate of ethylene agreed within 5% with the actual yield measured by the weight of polymer after polymerization. The detailed procedures for polymerization are described elsewhere by Kim et al. [4].

RESULTS AND DISCUSSION

The decay in polymerization rate after the buildup period might be attributed to such factors as catalyst deactivation, loss of active sites, intraparticle monomer diffusion through the growing polymer layer, and inefficient heat transfer from the polymer particle to bulk fluid. Some sound experiments rule out the possibility that the initial decay of the rate of polymerization (R_p) is attributed to limitation of monomer diffusion to the active sites through the barrier of crystalline polymer which encapsulates the catalyst. Keii et al. [2] and Doi et al. [9] demonstrated that the decrease of R_p versus time is not affected by intermittent removal and reintroduction of monomer. In other words, the decay of the rate of polymerization continues even when there is no polymerization. The second evidence is the comparison of R_p versus time (Chien and Kuo [10]) for polymerization of propylene with that of 1-decene, the stereoregular poly(1-decene) is soluble in heptane solvent at polymerization temperature of 50°C. The two systems showed the same decrease of R_p, i.e., the rate constant of deactivation obtained by second order plot of R_p versus time agreed within ±10%. Kim and Woo [11] argued against diffusion limitation by measuring the number of active sites (C*) at different polymerization times by CO inhibition method. Kim and Woo [11] concluded that the decrease of R_p is caused by the decrease of C*. Other less direct evidence such as the lack of effect of titanium concentration on the catalyst efficiency (Duck et al. [12]) and that the rate of catalyst deactivation is not related to productivity (Giannini [1]) was also published to argue against diffusion limitation.

Most of the experimental results can be analyzed according to the kinetics of second order decay with respect to [C*]. For very short propylene polymerization times (10 min) the decay rate has been said to be better described by third order kinetics [2]. However, we note that Kashiwa and Yoshitake [13] found no loss of R_p during the first 60 sec of propylene polymerization for $MgCl_2$ supported catalysts. At high temperatures, the initial rapid second order decay is followed by a first order decay or another slower second order process as reported by Keii et al. [2] and Chien and Kuo [10]. For the polymerization at low Al/Ti ratio, Chien and Kuo [10] found first order decay of R_p.

Under the assumptions that:

(1) the decrease of R_p from the relation $R_p = k_p C^*[M]$ is due to the decrease of C*,

(2) both k_p and [M] remain constant,

(3) all active sites are formed at the start of polymerization reaction, and

(4) no new sites are formed during polymerization, the deactivation of the active sites of the present catalyst combined with $AlEt_3$ as a cocatalyst followed the first order deactivation,

$$d[C^*]/dt = -k_d'[C^*]$$

where k_d' is a deactivation rate constant. This equation can be rewritten using the relation $R_p = k_p[C^*][M]$ as follows.

$$R_{p,t}/R_{p,o} = \exp(-k_d' t)$$

where, $R_{p,t}$: rate at time t

$R_{p,o}$: maximum polymerization rate.

From the slope of a linear plot of $\ln(R_{p,o}/R_{p,t})$ versus time, the value of k_d' can be obtained.

Figure 1 shows $\ln(R_{p,o}/R_{p,t})$ vs. t for various $AlEt_3$ concentrations. The first order decay law fits the polymerization data very well. The decay rate constants calculated from the slope of the plot in Fig. 1 with different $AlEt_3$ concentrations are summarized in Table 1. At the low concentration of $AlEt_3$ (0.12 mmol/l), the time to reach at the maximum polymerization rate is 34 min. The polymerization rate decay very rapidly after obtaining the maximum rate. The reactivation of active sites with $AlEt_3$ is very slow at low $AlEt_3$ concentration resulting in the large decay rate constant, $2.35 \times 10^{-2} min^{-1}$. In other words, the unexpected large decay rate constant may be due to the fact that a much larger fraction is used for scavenging trace quantities of O_2 and H_2O and less is available for site activation. At the concentration of $AlEt_3$ higher than 0.48 mmol/l, the decay rate constants are smaller than that at the $AlEt_3$ concentration of 0.12 mmol/l as shown in Table 1. This can be explained by the fact that above 0.48 mmol/l of $AlEt_3$ concentration, there are enough $AlEt_3$ to reactivate the deactivated active sites in the polymerization reactor. However, it is interesting to notice that the decay rate constant slightly increased with the increase of the concentration of $AlEt_3$ above 0.48 mmol/l of $AlEt_3$ concentration. This might be due to

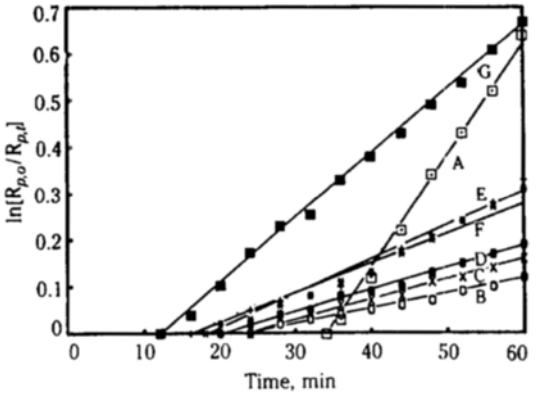

Fig. 1. First-order kinetic plot of decay of R_p with time at various $AlEt_3$ concentrations (mmol/l).
Polymerization conditions: T = 80°C; P = 12.4 atm; [Ti] = 1.785×10^{-5} mol/l: (A) 0.12; (B) 0.48; (C) 0.72; (D) 0.92; (E) 1.93; (F) 4.35; (G) 10.38 mmole/l.

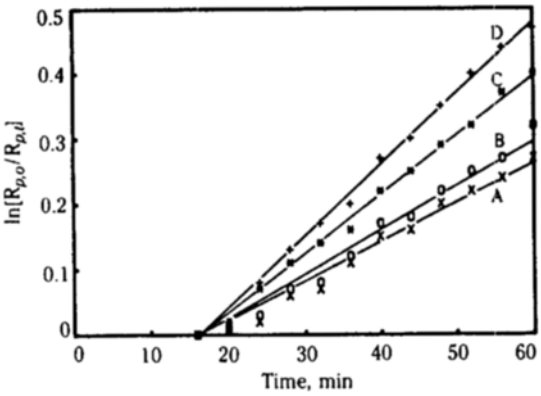

Fig. 2. First-order kinetic plot of decay of R_p with time at various ethylene pressures.
Polymerization conditions: T = 80°C; [Ti] = 1.785×10^{-5} mol/l; [$AlEt_3$] = 3.6 mmol/l: (A) 4.0; (B) 6.0; (C) 9.6; (D) 12.4 atm.

Table 1. Dependence of the polymerization rate and decay rate constant on the concentration of $AlEt_3$

[A] mmol/l	Al/Ti	$R_{p,o}$ [kg PE/g Ti hr]	$R_{p,60min}$ [kg PE/g Ti hr]	$t(R_{p,o})$* min	$k_d' \times 10^2$ min^{-1}
0.12	6.7	23	15	34	2.345
0.48	26.9	80	75	26	0.333
0.72	40.3	155	140	26	0.420
0.92	51.5	205	170	24	0.461
1.93	108.1	230	180	18	0.713
4.35	243.7	230	173	16	0.643
10.38	581.5	160	80	12	1.375

*The time to reach the maximum rate.

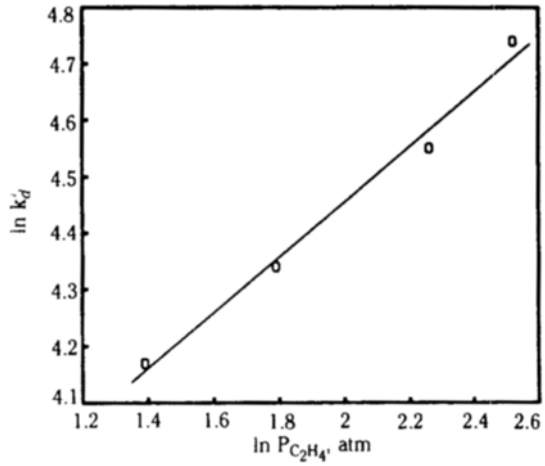

Fig. 3. Variation of ln k_d' of Fig. 2 with ln $P_{C_2H_4}$.

the deactivation by the poisoning effect of excess $AlEt_3$ which will coordinate strongly to the active sites preventing the monomer from being coordinated to the active sites or due to the over-reduction of active titanium species below the oxidation state of 2. Keii et al. [2] showed that the polymerization of propylene with $MgCl_2/TiCl_4/C_6H_5COOC_2H_5$ combined with $AlEt_3$ was based on the second order deactivation kinetics, while $TiCl_3/AlEt_3$ catalyst was deactivated based on the first order kinetics as reported by Keii et al. [6]. However, there was no report on the k_d' in the ethylene polymerization to be compared with.

It has also been realized that monomer can participate in the catalyst deactivation process. Monomer itself coordinated to the Ti active center causing the decrease in the concentration of polymerization propagation center. Monomer also can participate in the chain transfer reaction causing the polymerization rate to decrease because the chain transfer rate is usually less than the propagation rate. The first-order R_p deactivation plots at various ethylene pressures are shown in Fig. 2. Decay rate constants at the ethylene pressure of 4.0, 6.0, 9.6, 12.4 atm calculated from the slope of Fig. 2 are 5.9×10^{-3}, 6.6×10^{-3}, 9.1×10^{-3}, and 10.7×10^{-3} min^{-1}, respectively. As the pressure of ethylene increased, decay rate constant increased indicating that monomer is also involved in the deactivation process. To find the kinetic order with respect to monomer concentration, ln k_d' versus ln $P_{C_2H_4}$ are plotted in Fig. 3, and the slope is found to be 0.49. Accordingly, the deactivation rate constants

caused by monomer can be expressed as follows:

$$k_d' = C[M]^{1/2}$$

where C is a proportional constant.

Chien and Kuo [7] derived the same relation from the second order deactivation kinetics for the polymerization of propylene with $MgCl_2$/EB/PC/$AlEt_3$/$TiCl_4$-3$AlEt_3$/MPT catalyst. On the other hand, Kohara et al. [8] explained that k_d' was proportional to monomer concentration for the polymerization of propylene with $TiCl_3$/$AlEt_2X$ (X = Cl, Br, I) catalyst, i.e.,

$$k_d' = C[M].$$

The mechanisms of deactivation of catalytic sites are extremely difficult to elucidate for heterogeneous catalysts. For the classical Ziegler-Natta catalysts the active sites are so few that any trace amount of impurities or inhibitors produced during the activation or polymerization may poison them. With the increase in the number of active sites in the $MgCl_2$ supported catalysts, it is still doubtful that the mechanism of deactivation can be elucidated because the nature of chemisorbed species is not known. However, some plausible speculations may be possible. For the monomer assisted catalytic site deactivation the rate is proportional to $[M]^{1/2}$ as shown above. Therefore, the monomer adsorbed with the surface (s) is probably dissociated as follows

$$C_2H_4\,(s) \rightleftharpoons F\,(s) + G\,(s).$$

If F is a vinyl radical (s) and G is H·(s) then the deactivation may be represented by

$$P\text{-}Ti^{*}\,(s) + CH_2{=}CH\cdot\,(s) \rightarrow P\text{-}Ti\text{-}CH{=}CH_2\,(s)$$

$$P\text{-}Ti^{*}\,(s) + H\cdot\,(s) \rightarrow P\text{-}Ti\text{-}H\,(s).$$

Vinyl groups in the polymer end and Ti-H bond are often identified in the Ziegler-Natta polymerization. In the above process the inactive species are Ti(IV). Alternatively, the process could be reductive, i.e.,

$$P\text{-}Ti^{*}\text{-}Cl\,(s) + CH_2{=}CH\cdot\,(s) \rightarrow P\text{-}Ti\,(s) + CH_2{=}CHCl$$

$$P\text{-}Ti^{*}\text{-}Cl\,(s) + H\cdot\,(s) \rightarrow P\text{-}Ti\,(s) + HCl.$$

If F is ·CH=CH· and G is H_2, then the deactivation may be via oxidative coupling.

$$2P\text{-}Ti^{*}(s) + \cdot CH{=}CH\cdot \rightarrow P\text{-}Ti\text{-}CH{=}CH\text{-}Ti\text{-}P\,(s)$$

It would be rather difficult to ascertain what kind of the change in oxidation state occurs during the deactivation of Ti sites. Redox titration technique used to determine the Ti oxidation states in the catalyst developed by Chien and Wu [14] cannot be applied to the catalyst

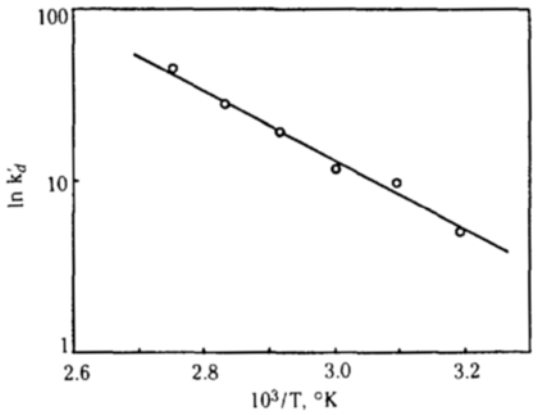

Fig. 4. Arrhenius plot of k_d' versus 1/T: Ti = 1.785 × 10^{-4} mol/l, P = 12.4 atm, and [$AlEt_3$] = 3.6 mmol/l.

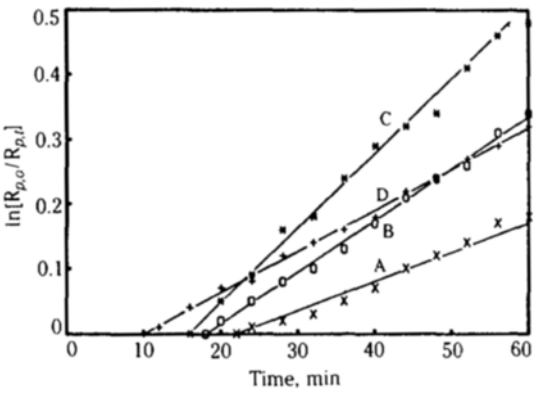

Fig. 5. First-order kinetic plot of deactivation of R_p with polymerization time at various hydrogen partial pressures.

Polymerization condition: T = 80°C; [Ti] = 1.785 × 10^{-5}; [$AlEt_3$] = 3.6 mmole/l; (A) 0.0; (B) 1.4; (C) 2.8; (D) 4.0 atm.

encapsulated with polymer. Methods such as ESCA or EXAF would require high vacuum which may alter the system. Indirect evidence obtained with our model systems suggested that internal olefins may be involved with decay by monomer.

Fig. 4 shows an Arrhenius plot for the activation energy of deactivating process. The activation energy for the deactivation reaction is 9.8 kcal/mole at the range of temperature from 50 to 90°C. This value of activation energy is close to the value of that in propagation rate and larger than that of diffusion rate, indicating that deactivation process is mainly involved with chemical nature.

The mechanism of deactivation by hydrogen de-

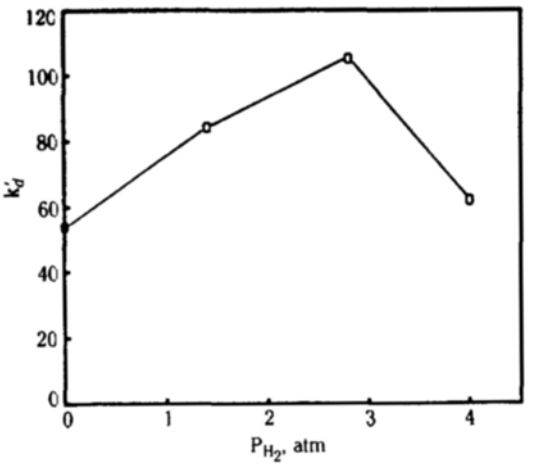

Fig. 6. Variation of k_d of Fig. 5 with P_{H_2}.

pends on the nature of the dissociated species of H_2 on the catalyst. Either oxidation, reduction, or formation of bridged hydrides could cause deactivation. The decay rate constants at the hydrogen pressures of 0, 1.4, 2.8, and 4.0 atm calculated from the slope of Fig. 5 indicate that they increased with the hydrogen pressure up to 2.8 atm and started to decrease above the hydrogen pressure of 2.8 atm (see Fig. 6). The effect of hydrogen on the rate of deactivation is shown in Fig. 5. The decay of R_p was accelerated as the partial pressure of hydrogen increased. The decay rate is maximum around the mole ratio of hydrogen to ethylene of 0.2. Hydrogen can be a poison in a sense that H_2 can be dissociatively adsorbed on the Ti active sites, resulting in the decrease of the polymerization active center and/or in the over-reduction of Ti species. The chain transfer rate due to H_2 is much less than the propagation rate, which reflects the decrease of polymerization rate, too.

CONCLUSION

Based on the fact that a decrease in the number of active centers was mainly associated with the decay, first order decay law fitted the polymerization rate data very well and that the decay rate constant was sensitive to the Al/Ti ratio. Decay rate constant was also sensitive to temperature in the range of 40-90°C. The activation energy for the deactivation reaction was 9.8 kcal/mole. For the monomer assisted catalytic site deactivation the rate was proportional to $[M]^{1/2}$. The deactivation by monomer has been thought to be related with some dissociative processes. The decay rate was maximum around the mole ratio of hydrogen to ethylene of 0.2.

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