Kinetic Study of Ethylene Polymerization by Highly Active Silica Supported TiCl$_4$ / MgCl$_2$ Catalysts

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Synopsis

The kinetics of ethylene polymerization 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 kg/cm^2. The role of MgCl$_2$ was discussed from the dependence of the Mg/Ti ratio on the catalytic activity. The polymerzation rate was first order with respect to the monomer concentration and the dependence of the polymerization rate on the concentration of Al(C$_2$H$_5$)$_3$ could be described by the Langmuir–Hinshelwood mechanism. The dependence of initial rate and the time to reach the maximum polymerization rate on the concentration of Al(C$_2$H$_5$)$_3$ was also discussed. Polymerization rates as a function of the polymerization temperature showed a maximum and the activation energy was 11.8 kcal/mol between 50 and 80°C. The polymerization rate decreased with the increase of hydrogen partial pressure. The active site concentration (C^*) was 1.9 × 10^{-2} mol/mol Ti by the inhibition method with carbon monoxide.

INTRODUCTION

While the catalytic polymerization of olefins has not been generally understood in a detailed mechanistic sense, significant technological advances based on new and improved catalysts have been made since the original discoveries of Ziegler–Natta catalysts. Developments toward highly active catalysts have been mainly based on the reactions among magnesium, titanium, and aluminum compounds. Most of highly active catalysts reported so far have been prepared by supporting TiCl$_4$ on the surface of milled MgCl$_2$. These supported catalysts continue to attract considerable attention and appear to be an object of study in many industrial and academic laboratories throughout the world.

Union Carbide Corp. has recently developed a new type of supported catalyst for the fluidized bed polymerization.[1] A precursor compound was prepared from titanium compound, magnesium compound, and electron donor compound. This precursor solution was impregnated onto the silica support materials for the preparation of their catalysts. However, detailed kinetic studies of ethylene polymerization catalyzed over this type of catalyst have not been published. Soga and co-workers prepared similar catalysts, SiO$_2$-supported MgCl$_2$/TiCl$_4$ combined with Al(C$_2$H$_5$)$_3$, and studied the copolymerization of ethylene with propylene.[2,3] They proposed a plausible model for the active species including the activating effect of MgCl$_2$.

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In the present paper, several important kinetic behaviors of the slurry-phase ethylene polymerization with $SiO_2/MgCl_2/TiCl_4$ catalyst combined with $Al(C_2H_5)_3$ will be discussed. The present work was carried out in the broad range of pressure and temperature close to commercial ethylene polymerization conditions.

EXPERIMENTAL

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 5A/13X. Ultra high purity grade of carbon monoxide (Matheson, U.S.A.) was used for the active site measurement 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., U.S.A.) was purified by refluxing with $LiAlH_4$ for several hours.

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

Catalyst Preparation

To a 250-mL glass reactor equipped with a magnetic stirrer were added 5.0 g of silica gel, which had been dehydrated at 500°C *in vacuo* for 12 h and 0.5 g of $TiCl_4$ solution in *n*-hexane at room temperature. After raising the temperature to 60°C, the mixture was stirred vigorously for 3 h, filtered under nitrogen, washed solid portion with plenty of *n*-hexane, and then dried under nitrogen purge at 60°C for 6 h to assure free flowing powder. This prepared catalyst ($TiCl_4/SiO_2$) was transferred to a glass tube inside a glove box and sealed off with a torch outside, and then stored in the N_2 atmosphere before use.

Alternatively, to a 250-mL glass reactor containing 50 mL of electron donor (THF) was added an appropriate amount of anhydrous $MgCl_2$. The mixture was kept standing with vigorous stirring until $MgCl_2$ was completely dissolved at 60°C. To this mixture, 0.5 g of $TiCl_4$ was added dropwise at 60°C over 15 min under stirring. This yellow precursor solution was impregnated to 5 g of silica gel dehydrated at 500°C under vacuum above. The precipitate was dried under a nitrogen purge at 60°C for 6 h.

The surface areas of dehydrated silica and supported catalysts were determined by the conventional BET method. Titanium contents of the catalysts were determined colorimetrically with a UV-VIS spectrophotometer [Beckman Model 35].

Polymerization

Slurry polymerization was carried out in a 1 l Parr reactor (Series 4520) with a turbine type impeller, a serpentine cooling coil, and a deep tube to
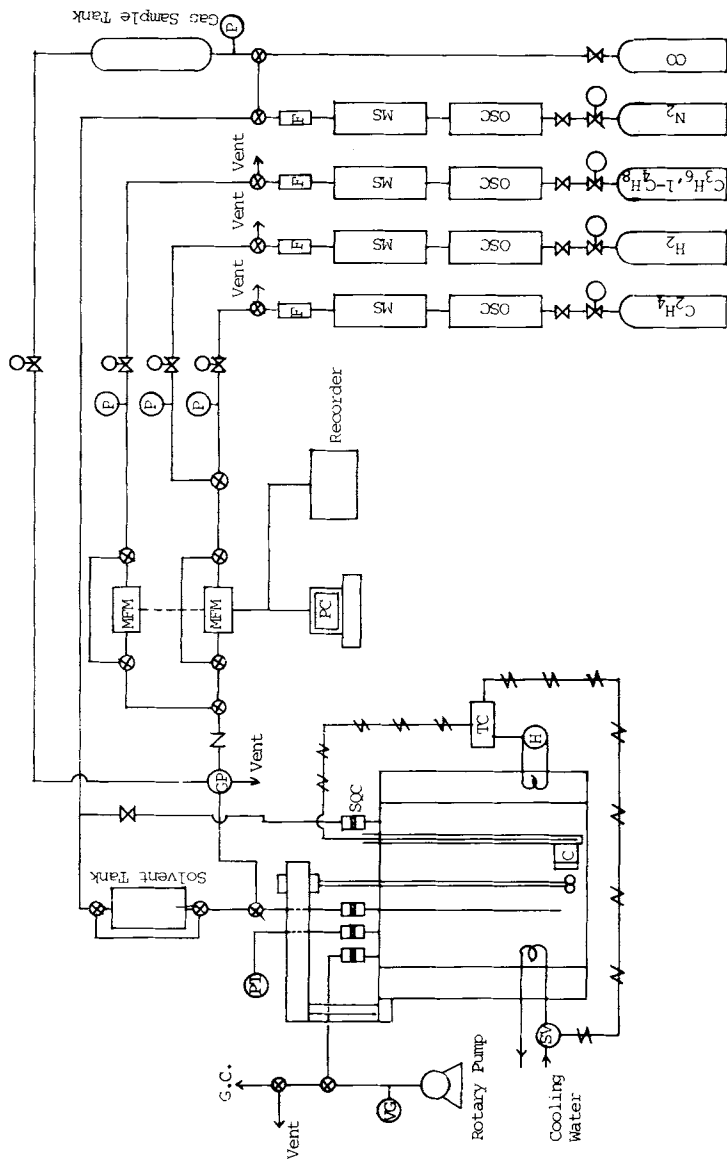
Fig. 1.   High-pressure polymerization unit: (C) catalyst vial; (F) filters; (GP) six-port sampling valve; (H) heater; (MFM) mass flow meter; (MS) molecular sieves; (OSC) oxygen scavenging columns; (P) pressure gauges; (PC) personal computer; (PT) pressure transducer; (SQC) series quick connectors; (SV) solenoid valve; (TC) temperature controller; (VG) vacuum gauge.

introduce monomer under constant pressure of ethylene. The apparatus is shown in Figure 1.

In order to obtain reproducible results (within $\pm 5\%$) it was considered essential to prepare polymerization mixtures in an identical manner. All the components of polymerization were made up in the same manner and mixed in the same order. A glass ampoule containing a catalyst was installed in the reactor. A prescribed amount of $AlEt_3$ and 500 mL of n-hexane were introduced into the reactor under nitrogen stream. After evacuation, etylene was introduced at the polymerization temperature. When hydrogen was used, the reactor was first charged with hydrogen to the desired hydrogen partial pressure, and then the total pressure was raised to the desired polymerization pressure by adding monomer. When no more absorption of ethylene to n-hexane was observed, polymerization was started by breaking the glass ampoule containing the prescribed amount of catalyst.

Polymerization mixture was stirred at the speed of 800 rpm in order to avoid the effect of monomer diffusion through the gas–liquid interface. The temperature of polymerization controlled within $\pm 0.5°C$. The polymerization rate was determined at every 0.01 s from the rate of ethylene consumption, measured by a hot-wire flow meter (Model 5850D from Brooks Instrument Div.) connected to a personal computer through an A/D converter. Polymer yield estimated from the consumption rate of ethylene agreed within $\pm 2.5\%$ with the yield measured by the weight of polymer produced after polymerization. A known amount of CO was injected into the polymerization reactor through a six-port sampling valve and the decrease in the overall rate of polymerization was measured simultaneously in order to determine the number of active centers.[4,5]

Molecular weights of prepared polymer were determined with GPC (Waters Model 150-C) utilizing a universal calibration method calibrated with a standard polystyrene. A GPC chromatogram was recorded at 135°C using trichlorobenzene as a solvent.

RESULTS AND DISCUSSION

The Role of $MgCl_2$

Table I shows the activities of ethylene polymerization dependent on the ratio of Mg/Ti. Similar to the case of propylene polymerization by $TiCl_4/MgCl_2/SiO_2$,[3] activity was sharply increased by the presence of a small quantity of $MgCl_2$, reached the maximum around the mole ratio of Mg/Ti of 2, and slightly decreased at the mole ratio of Mg/Ti larger than 2. This result indicated that the highest activity comes from the formation of bimetallic Mg/Ti complex (Mg/Ti = 2). The enhancement in the catalytic activity of $TiCl_4$ with the addition of $MgCl_2$ was well discussed by Karol.[6] Greco and co-workers reported that Ti–Mg complexes have well-defined stoichiometry, ionic character, and crystalline structure and that $(MgCl_2)_{1.5}TiCl_3$ treated with $(i\text{-}C_4H_9)_3Al$ was found to be very active in ethylene polymerization.[7]
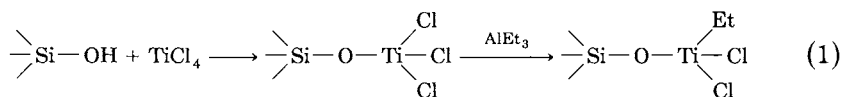
$TiCl_4/MgCl_2/SiO_2$ catalyst of the present study was prepared by anchoring Ti/Mg bimetallic complex to the surface of silica gel. The mode of reaction between the hydroxyl groups of silica gel and bimetallic halides will

TABLE I
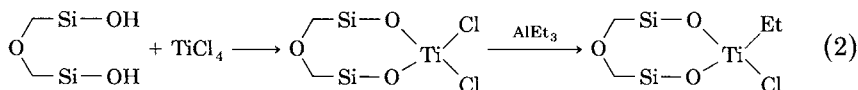Surface Area and Catalytic Activity with the Mole Ratio of Mg/Ti[a]

Catalyst	[Mg]/[Ti]	Surface area (m^2/g)	Activity (kg PE/g Ti h)
TiCl$_4$/SiO$_2$	0	212	5.4
TiCl$_4$/MgCl$_2$/SiO$_2$	0.5	192	24.6
TiCl$_4$/MgCl$_2$/SiO$_2$	1.0	178	51.2
TiCl$_4$/MgCl$_2$/SiO$_2$	2.0	188	184
TiCl$_4$/MgCl$_2$/SiO$_2$	3.0	180	175
TiCl$_4$/MgCl$_2$/SiO$_2$	5.0	174	169

[a] Polymerization time = 1 h, P = 9.2 kg/cm^2, T = 80°C, Al/Ti = 140.

affect the catalytic activity of the prepared catalyst. The plausible mechanism of the reaction of SiO$_2$ with TiCl$_4$ was previously proposed by several authors.[3,8,9] According to their results, the preparation of silica-supported TiCl$_4$ catalyst was based on the reaction of TiCl$_4$ with hydroxyl groups of the silica as follows:

$$\text{Si}-\text{OH} + \text{TiCl}_4 \longrightarrow \text{Si}-\text{O}-\underset{\text{Cl}}{\overset{\text{Cl}}{\text{Ti}}}-\text{Cl} \xrightarrow{\text{AlEt}_3} \text{Si}-\text{O}-\underset{\text{Cl}}{\overset{\text{Et}}{\text{Ti}}}-\text{Cl} \qquad (1)$$

single isolated hydroxyl group

$$\begin{array}{c}\text{Si}-\text{OH}\\ \text{O}\\ \text{Si}-\text{OH}\end{array} + \text{TiCl}_4 \longrightarrow \begin{array}{c}\text{Si}-\text{O}\\ \text{O} \quad \text{Ti}\begin{array}{c}\text{Cl}\\ \text{Cl}\end{array}\\ \text{Si}-\text{O}\end{array} \xrightarrow{\text{AlEt}_3} \begin{array}{c}\text{Si}-\text{O}\\ \text{O} \quad \text{Ti}\begin{array}{c}\text{Et}\\ \text{Cl}\end{array}\\ \text{Si}-\text{O}\end{array} \qquad (2)$$

isolated pairs of hydroxyl group

Chien and Hsieh found that the titanium chloride anchored to single isolated hydroxyl groups can be reduced to the active species effective for the propylene polymerization.[8] Soga and co-workers obtained a similar result by the ESR study[3], while Munoz-Escalona et al. proposed that adjacent two hydroxyl groups played a role in forming active species for the ethylene polymerization.[9]

Soga and co-workers also proposed a plausible mechanism of the active species formed from the TiCl$_4$/MgCl$_2$/SiO$_2$/AlEt$_3$ catalyst system, where the catalyst was prepared by reacting SiO$_2$ with TiCl$_4$ first then with MgCl$_2$ dissolved in THF. They confirmed that MgCl$_2$ forms a weak complex with the titanium species onto the single isolated hydroxyl groups of silica. The most active catalyst was obtained at the atomic ratio of Mg/Ti of 2. The less active catalyst was obtained when MgCl$_2$ complexed with TiCl$_4$ anchored to the isolated pairs of hydroxyl groups on silica. In the present study, active precursor solid solution prepared from dissolving MgCl$_2$ and TiCl$_4$ in THF reacted with the hydroxyl groups of the silica as shown in Figure 2. Species (A) can react with one hydroxl group to form species (C) on the surface of silica gel, because the bridged chlorine is less active than terminal chlorine in the reaction with hydroxyl groups. However, species (B) having Mg/Ti ratio
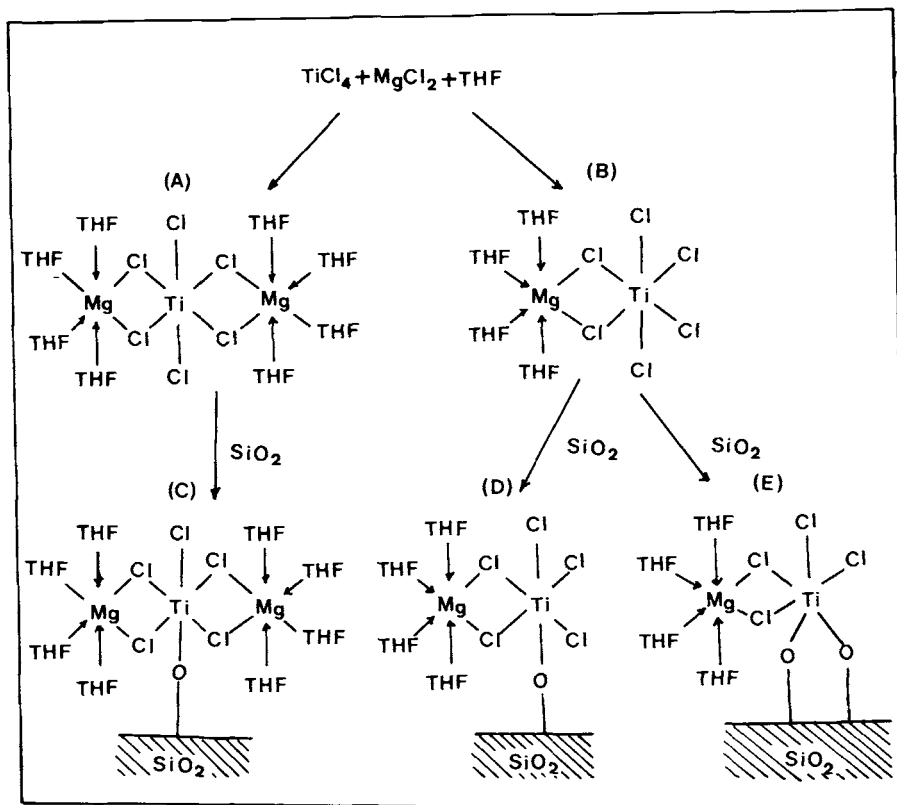
Fig. 2. Plausible structure of Mg/Ti bimetallic complexes attached to the surface of silica gel.

of 1 (or less than 1) has more terminal chlorine atoms than species (A), resulting in the surface complex of species (D) and (E). Bidendate complex (E) is less active in ethylene polymerization than monodendate complexes, (C) and (D) as reported previously.[3,8] Species (B) of Mg/Ti ratio of 1 is found to be less active than species (A) in the ethylene polymerization.[10] When the ratio of Mg/Ti in the complex decreased, the catalytic activity decreased due to the more formation of bidendate bimetallic complex and the less catalytic activity of Mg/Ti bimetallic complex itself. However, further dilution of $TiCl_4$ with $MgCl_2$ (Mg/Ti > 2) did not change the specific activity of titanium compound much because the extent of dilution of $TiCl_4$ with $MgCl_2$ is not changed much above the Mg/Ti ratio of 2.

The surface area of prepared $TiCl_4/MgCl_2/SiO_2$ catalyst was 40–60% of that of unsupported silica used as a support materials, because the reaction of bulky Mg/Ti bimetallic complexes with hydroxyl groups on the surface silica will block the pores of small diameter, ca. < 80 Å. The number density of hydroxyl group is dependent on the dehydroxylation temperatures. Hence the choice of dehydroxylation temperature will affect the extent of the formation of bidendate complexes such as species (E) in Figure 2. The number of hydroxyl groups per 100 $Å^2$ in the surface of silica was found to be 2 after dehydroxylation of silica at 500°C.[11]

Elimination of the Effect of Mass Transfer Resistance

In order to find out whether an external mass transfer resistance is present during polymerization, polymerization rates were measured in the same polymerization condition except for the stirring speed and the amounts of catalyst. Above 800 rpm, the polymerization rate did not change, indicating that there was no external mass transfer resistance. The polymerization rate was linearly proportional to the amount of catalyst when the concentration of catalyst in terms of Ti content was less than 2.5×10^{-5} mmol/L. In our study, the concentration of Ti was 1.785×10^{-5} mmol/L. Hence, the polymerization rate was kept less than the rate of transport of gas phase ethylene to the liquid polymerization mixture. With these results, it can be concluded that external gas–liquid transfer resistance is not present in our polymerization conditions.

In order to find out internal mass transfer resistance (or diffusion limitation) in the porous catalyst, the Thiele modulus, characteristic of the ratio of an intrinsic polymerization rate in the absence of mass transfer limitations to the rate of diffusion into the pore under reaction conditions, was calculated according to the following equation[12]:

$$\phi = \left(\frac{k_p C_0}{D_m} \right)^{1/2} S_0$$

where ϕ = Thiele modulus, C_0 = initial concentration of active center, D_m = diffusivity of ethylene (cm^2 s^{-1}), k_p = propagation rate constants (mol^{-1} s^{-1}), and S_0 = initial radius of catalyst particle.

For TiCl$_4$/MgCl$_2$/SiO$_2$ catalyst, $\phi = 1.25 \times 10^{-3}$ by using $D_m = 35 \times 10^{-6}$ cm^2/s^{-1} and $S_0 = 3 \times 10^{-6}$ cm^{12} for $k_p = 1.8 \times 10^4$ 1/mol s and $C_0 = 1.9 \times 10^{-2}$ mol C*/mol Ti. A large value of ϕ (> 10) will indicate the presence of a diffusion limitation, while a small value of Thiele modulus less than 1 indicates the absence of a diffusion limitation. The value of Thiele modulus in the present polymerization condition is 1.25×10^{-3}, which is small enough to neglect the internal diffusion limitation. Accordingly, it can be concluded that our polymerization reaction conditions are not involved with a mass transfer resistance.

Effect of Ethylene Pressure on Polymerization Rate

Figure 3 shows the polymerization rate curves obtained with TiCl$_4$/MgCl$_2$/SiO$_2$ catalyst (Mg/Ti = 3.0) at four different monomer pressures. From the average polymerization rates over 1 and 2 h, it is found that polymerization is a first-order reaction with respect to the pressure of ethylene as shown in Figure 4. The maximum rates $R_{p,\text{max}}$, are also proportional to ethylene pressures.

Effect of Aluminium Cocatalyst Concentration on Polymerization Rate

Figure 5 shows the polymerization rate curves at various concentrations of AlEt$_3$ at 80°C and at the ethylene pressure of 9.6 kg/cm^2. As the concentra-
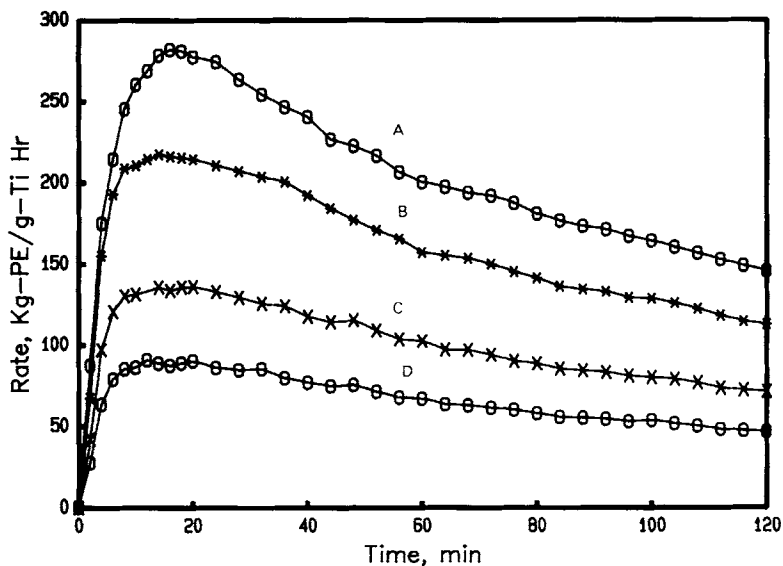
Fig. 3. Effect of monomer pressures on polymerization rate. Polymerization conditions: $T = 80°C$; catalyst weight $= 0.05$ g ([Ti] $= 1.785 \times 10^{-5}$ mol); [AlEt$_3$] $= 3.6$ mmol/L: (A) 12.4; (B) 9.6; (C) 6.0; (D) 4.0 kg/cm^2.

tion of cocatalyst increased, the time to reach the maximum rate decreased, and the rate started to decrease above the concentration of AlEt$_3$, 4.35 mmol/L. The time to reach the maximum rate decreased with the increase in the concentration of cocatalyst. The kinetic behavior of olefin polymerization during the initial period of polymerization is strongly affected by the order of addition of AlEt$_3$ and monomer to the catalyst. In the present study, a given
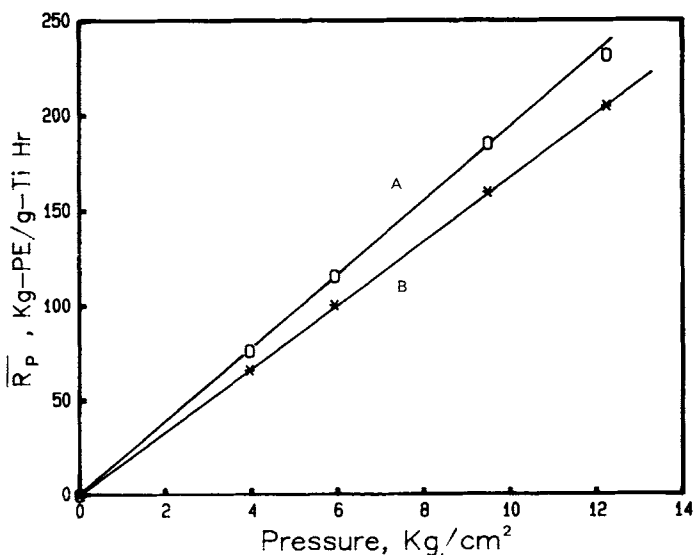
Fig. 4. Dependences of polymerization rate on the monomer pressures. Polymerization conditions are the same as those in Figure 3. Polymerization time: (A) 1 h; (B) 2 h.
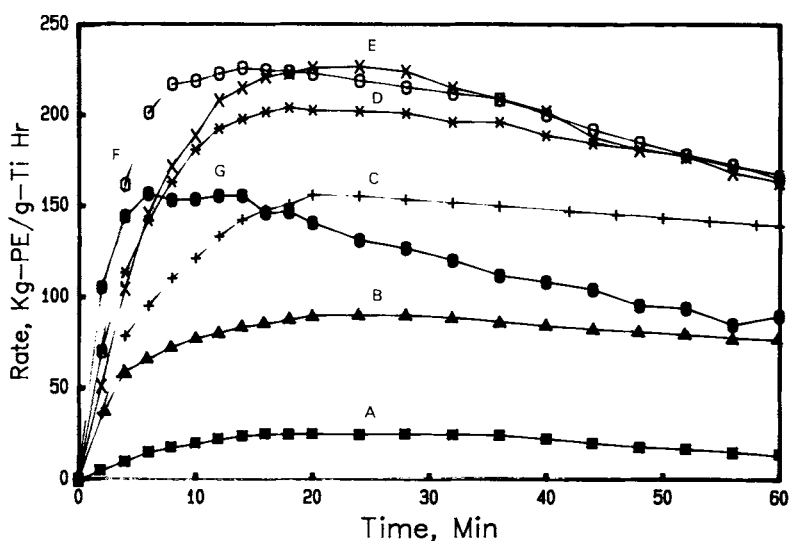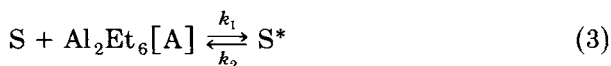
Fig. 5. Effect of Al(C$_2$H$_5$)$_3$ concentration on polymerization rate. Polymerization conditions: $T = 80°C$; $P = 12.4$ kg/cm^2; [Ti] $= 1.785 \times 10^{-5}$ mol; (A) 0.12; (B) 0.48; (C) 0.72; (D) 0.92; (E) 1.93; (F) 4.35; (G) 10.38 mmol/L.

amount of AlEt$_3$ and monomer were first introduced into the reactor, and then the catalyst ampoule containing the prescribed amount of catalyst was broken at the beginning of polymerization. Upon contacting the catalyst to AlEt$_3$ and monomer, a competitive adsorption on surface sites (S) between monomer and AlEt$_3$ to form active sites (S*), was followed by the formation of a polymerization center (C*) as shown in the following reactions:

$$S + Al_2Et_6[A] \underset{k_2}{\overset{k_1}{\rightleftarrows}} S^* \qquad (3)$$

$$S + C_2H_4[M] \underset{k_4}{\overset{k_3}{\rightleftarrows}} S^* \qquad (4)$$

$$S^* + Al_2Et_6 \overset{k_5}{\longrightarrow} C^* \qquad (5)$$

$$S^* + C_2H_4 \overset{k_6}{\longrightarrow} C^* \qquad (6)$$

where k_1, k_2, k_3, k_4, k_5, and k_6 are the proportional rate constants, K$_A$ and K$_M$ are the adsorption equilibrium constants of AlEt$_3$ and the monomer, respectively, [A] = concentration of AlEt$_3$, and [M] = monomer concentration.

The rate of formation of polymerization centers can be approximated as follows:

$$dC^*/dt = k_5[S^*][A] + k_6[S^*][M]$$

$$= (k_5 + k_6K_A/K_M)[S^*][A] \qquad (7)$$

Substituting $[S^*] = [S^*]_0 - [C^*]$ and solving eq. (7) we obtain

$$C^* = [S^*]_0\{1 - \exp[-(k_5 + k_6 K_A/K_M)[A]t]\} \tag{8}$$

At the beginning of polymerization, where $t \simeq 0$, eq. (8) may be approximated using the relation $R_p = k_p C^*[M]$ and $R_{p0} = k_p[M][S^*]_0$ as follows:

$$R_p = k_p[S^*]_0(k_5 + k_6 K_A/K_M)[M][A]t \tag{9}$$

Provided that $k' = k_p(k_5 + k_6 K_A/K_M)[S^*]_0 H$, where H is Henry's constant, the following relation for the initial polymerization rate is obtained:

$$R_p = k'P[A]t \tag{10}$$

Equation (10) indicates that the initial rate of polymerization depends on the pressure of monomer and on the concentration of $AlEt_3$. The initial rate increases as the concentration of $AlEt_3$ increases at constant monomer pressure (Fig. 5) and can be fitted using eq. (10). This indicates that the activation of titanium species by $AlEt_3$ is a rate-determining step for the formation of polymerization centers during the initial period of polymerization. Similar results were reported for propylene polymerization over Stauffer catalyst, in which polymerization was started by syringing $AlEt_3$ into the reactor containing a prescribed amount of catalyst and monomer dissolved in n-heptane.[13] The calculated value of k' from eq. (10) is about 1.7×10^5 g C_2H_4 L/ (g Ti h^2 mmol atm) using the data of Figure 5.

The activity of the catalyst is largely dependent on the nature of aluminum alkyl and the mole ratio of cocatalyst to catalyst. In our study, the maximum
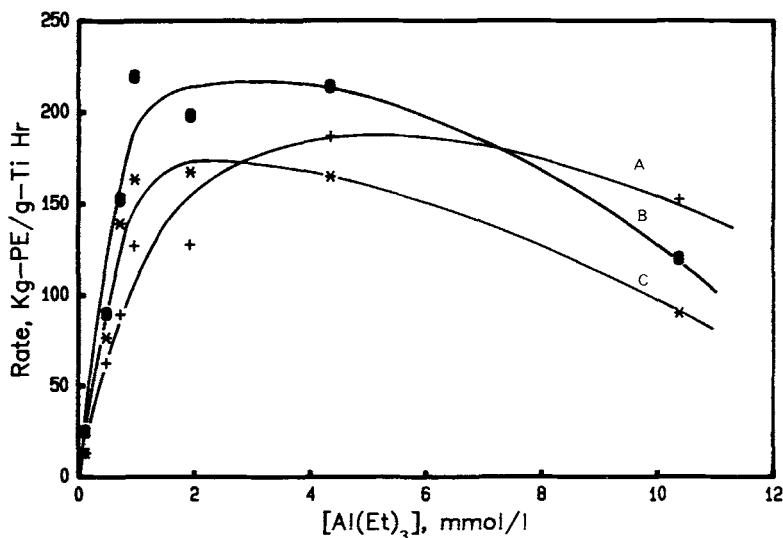

Fig. 6. Dependences of the polymerization rate on the concentrations of $Al(C_2H_5)_3$ at 5, 30, and 60 min. Polymerizations are the same as those in Figure 5. Polymerization time: (A) 5 min; (B) 30 min; (C) 60 min.
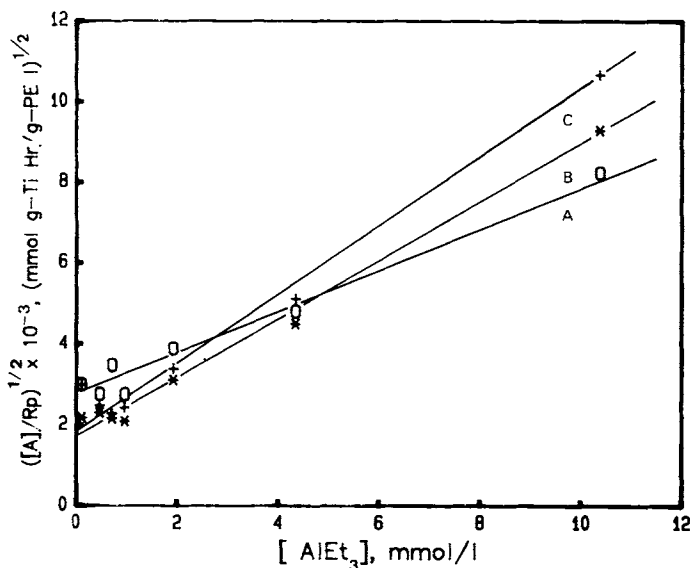
Fig. 7. Langmuir–Hinshelwood plot for the data in Figure 6. Polymerization time: (A) 5 min; (B) 30 min; (C) 60 min.

activity was observed at the concentration of AlEt$_3$ (Al/Ti $\approx$ 60), as shown in Figure 6. This can be explained by the conclusion of Zakharov and co-workers that some aluminum alkyl does not interact with titanium but was adsorbed on the silica surface in a manner ineffective for polymerization.[14] One possible explanation for the maximum rate at a certain AlEt$_3$ concentration is competitive adsorption on the same site between monomer and AlEt$_3$. The Langmuir–Hinshelwood mechanism, whereby both monomer and aluminum alkyl are adsorbed onto active sites, leads to the following equation:

$$R_p = \frac{kK_M K_A [A][M]}{\left(1 + K_A[A] + K_M[M]\right)^2} \tag{11}$$

If $K_A \gg K_M$, this can be rewritten at the constant monomer concentration as

$$R_p = k'\frac{K_A[A]}{\left(1 + K_A[A]\right)^2} \tag{12}$$

Figure 7 shows the plot of $([A]/R_p)^{1/2}$ against [A] at various polymerization times. Linear plots were obtained in the experimental range of Al/Ti ratio (30–600). Keii and co-workers interpreted the phenomena based on the changes in k' and K_A values.[4] The decrease in the k' value is mainly responsible for the rapid decrease of polymerization rate. However, in our catalyst system K_A was almost constant at 390 L/mol and k' was decreased to a less degree from 8.0×10^6 h^{-1} at 5 min to 6.0×10^6 h^{-1} at 60 min. This might be a reason why the polymerization rate of TiCl$_4$/MgCl$_2$/SiO$_2$ catalyst decreased slightly with polymerization time.

Effect of Polymerization Temperature on Polymerization Rate

The dependences of polymerization rates on the polymerization temperatures between 40 and 90°C is shown in Figure 8. Our catalyst system showed a complex temperature dependence of polymerization rate. The rate of polymerization increased as the temperature increased from 40 to 80°C. However, it decreased above 80°C. The increase in the initial rate was proportional to the polymerization temperature, indicating that the rate of active site formation is greatly dependent on the temperature. The time to reach the maximum rate is also dependent on the temperature. The initial polymerization rates increased slowly at 40, 50, and 60°C, and no conspicuous decay were observed for 2 h of polymerization.

Figure 9 shows the relation between $\log(R_p/[M])$ and $1/T$ at 1 and 2 h. The apparent activation energies calculated from the average rates over 1 h at 18.7, 13.6, and 14.3 kcal/mol at 40–50, 50–80, and 80–90°C, respectively. Those evaluated from average rates over 2 h are 16.8, 11.8, and -16.4 kcal/mol at the same temperature ranges. The activation energies obtained from the present study are slightly larger than those obtained from other catalyst systems as indicated in Table II.

Berger and Grieveson have observed similar temperature dependence to ours in the ethylene polymerization with $TiCl_3$–$AlEt_2Cl$ system and proposed a change of rate-determining step from a chemical reaction at lower temperatures to a monomer diffusion at higher temperatures.[18] On the contrary, Keii and co-workers proposed that the irreversible decrease of the number of polymerization centers at higher temperatures might be attributed to the negative activation energy.[13] The decrease of polymerization rate above 80°C may not be a result of kinetic phenomena alone. Floyd and co-workers
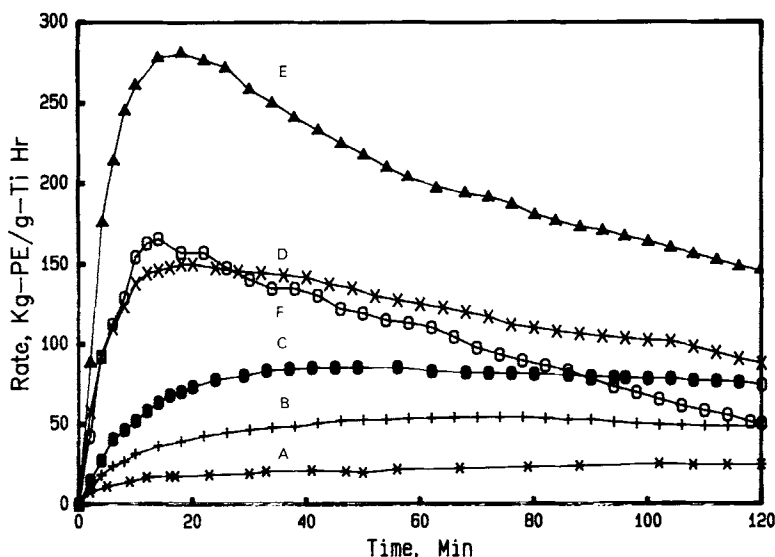

Fig. 8. Effect of temperature on the polymerization rate. Polymerization conditions: $P = 12.4$ kg/cm²; [Ti] $= 1.785 \times 10^{-5}$ mol; [AlEt$_3$] $= 3.6$ mmol/L: (A) 40; (B) 50; (C) 60; (D) 70; (E) 80; (F) 90°C.
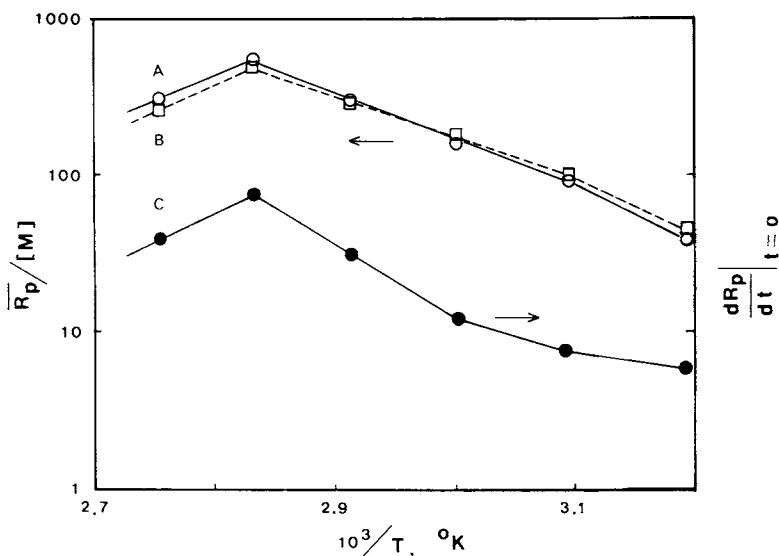
Fig. 9. Arrhenius plot of the average polymerization rate and initial polymerization rate extrapolating to zero time. Polymerization conditions are the same as those in Figure 8. Polymerization time: (A) 1 h; (B) 2 h; (C) 0 h.

presented an accurate model to estimate the importance of mass transfer resistance in solid catalyst systems.[19] They suggested that a catalyst is diffusion-limited, if the Arrhenius plot for the initial rate, obtained by extrapolating the polymerization rate to zero time, differs from the Arrhenius plot for long-time yield. Considering their model and the morphology of catalyst, TiCl$_4$/MgCl$_2$/SiO$_2$ activated with AlEt$_3$, polymerization at higher temperature is somewhat diffusion-limited as shown in Figure 9, where the nonlinearity was observed. However, the drastic decrease in the rate above 80°C cannot be explained by the diffusion limitations. This must be due to the destruction of active sites above 80°C. The unsupported MgCl$_2$/TiCl$_4$/AlEt$_3$ catalyst showed relatively rapid decrease in the polymerization rate above 70°C.[20] The stabilization of active species anchored on silica gel is due to the decrease in the mobility of active species on the surface of silica gel, in which titanium

TABLE II
Activation Energies in Ethylene Polymerization by Various Catalyst Systems

Catalyst system	Temperature range (°C)	E (kcal/mol)
TiCl$_3$/SiO$_2$ + AlEt$_3$[15]	30–50	10.0
	50–90	3.0
TiCl$_4$/MgCl$_2$ + AlEt$_3$[16]	40–60	10.0
	60–90	4.5
TiCl$_3$/MgClBr + AlEt$_3$[17]	0–50	18.0
This work (over 2 h)	40–50	16.8
	50–80	11.8
	80–90	−16.4

active species are distributed onto the surface of silica gel by the reaction with hydroxyl groups.

Effect of Hydrogen

A kinetic investigation of polymerization of ethylene with the $TiCl_4/MgCl_2/SiO_2$ catalytic system at various partial pressures of hydrogen ranging from 0 to 4.0 kg/cm^2 was carried out at 80°C and 12.4 kg/cm^2 of ethylene partial pressure. As shown in Figure 10, the time to reach maximum rates decreased as the partial pressure of H_2 increased. In addition, the average polymerization rate decreases upon the addition of hydrogen as shown in Figure 11. It can be proposed from these results that catalyst has a site that can be activated by H_2, because the same amount of $AlEt_3$ (3.6 mmol/L) was added to the polymerization mixture and all the titanium species were not activated by $AlEt_3$. Furthermore, the polymerization rate is proportional to the concentration of H_2 at the early stage of polymerization. On the other hand, the maximum rates were depressed by the increase of the hydrogen partial pressure. This can be explained by the proposal that the catalytically active species activated by H_2 (Ti—hydride) is less active than the catalytically active species activated by $AlEt_3$. Further increase of hydrogen partial pressure did not decrease the polymerization rate much, because the excess amount of hydrogen cannot be used to form a [cat]—H bond.

Natta investigated the influences of hydrogen on molecular weight and on the rate of polymerization of ethylene and propylene with catalysts prepared from $AlEt_3$ and $TiCl_3$.[21] He found that the M_n decreased proportional to the square root of partial pressure of hydrogen in the following equation:

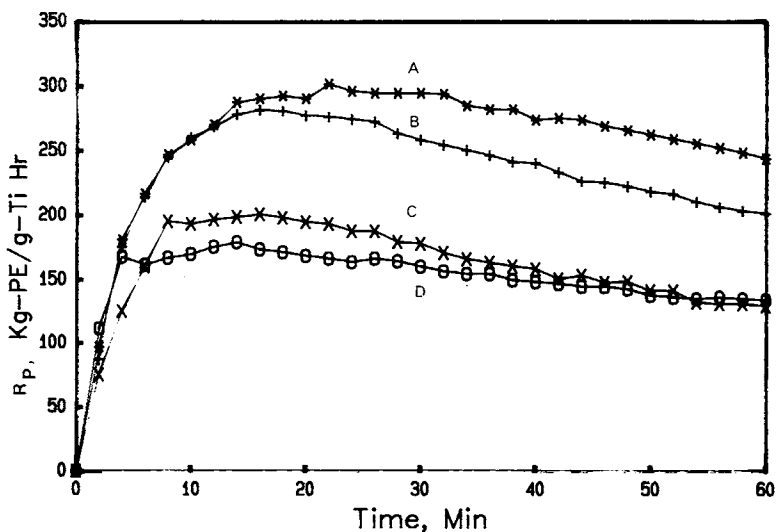$$M_n = 1\Big/\Big(K_1 + K_2[P(H_2)]^{1/2}\Big) \qquad (13)$$

Fig. 10. Effect of hydrogen partial pressures on the polymerization rate. Polymerization conditions: $T = 80°C$; $P = 12.4$ kg/cm^2; [Ti] $= 1.785 \times 10^{-5}$ mol; [AlEt$_3$] = 3.6 mmol/L: (A) 0.0; (B) 1.4; (C) 2.8; (D) 4.0 kg/cm^2.

TABLE III
Effect of Hydrogen Pressures on Molecular Weight of Polyethylene[a]

P_H	M_n	M_w	MWD
0.0	275,200	1,243.900	4.52
1.4	66,200	320,500	4.84
2.8	47,400	230,800	4.87
4.0	41,500	197,500	4.76

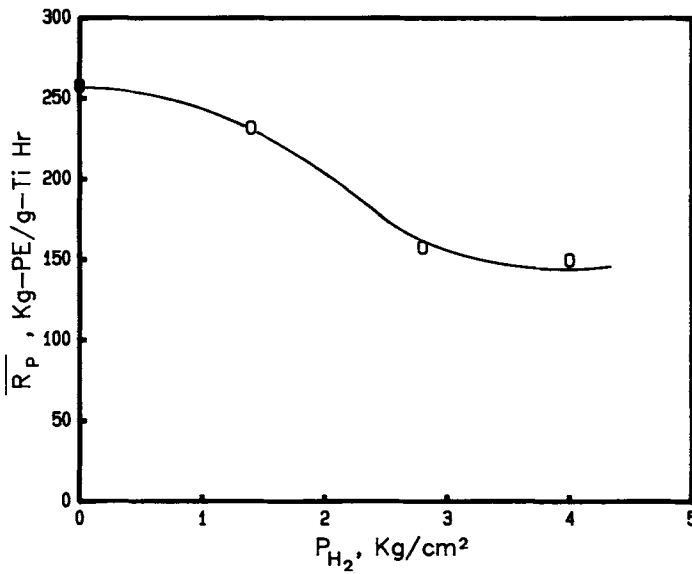[a] The polymerization conditions are the same as those in Figure 10.

Fig. 11. Effect of hydrogen on the average polymerization rate. Polymerization conditions are the same as those in Figure 10.
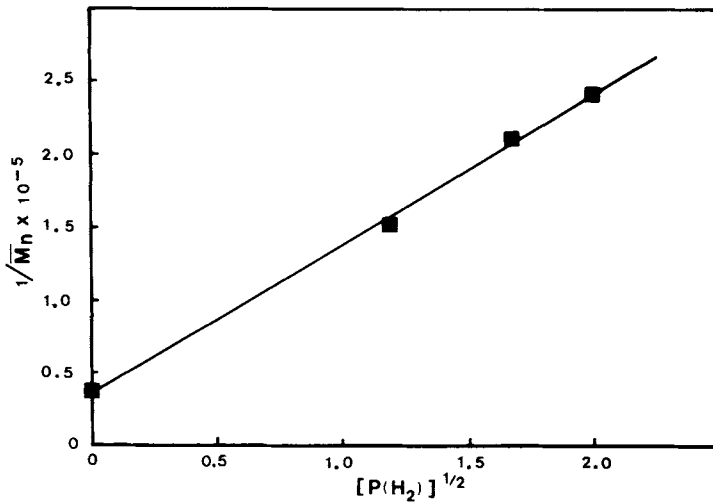

Fig. 12. Plot of $1/M_n$ vs. $[P(H_2)]^{1/2}$.

The M_n, M_w, and PDI of polyethylene after 1 h polymerization at different hydrogen partial pressures are shown in Table III. It can be seen that the average molecular weight decreased sharply as the hydrogen partial pressure increased, while polydispersity index (PDI) kept constant at around 4.8. From the plot of $1/M_n$ against $[P(H_2)]^{1/2}$, linear relationships were obtained as shown in Figure 12. With K_1 and K_2 obtained from Figure 12 the following equation was obtained:

$$M_n = 1\bigg/\Big(2.5 \times 10^{-6} + 1.1 \times 10^{-5}[P(H_2)]^{1/2}\Big) \qquad (14)$$

Hence, it can be concluded that the M_n of polyethylene obtained with silica supported $TiCl_4/MgCl_2$ catalyst also decreased according to the eq. (13).

Determination of the Active Site Concentration

A knowledge of the active site concentration C^* is required to evaluate the rate constant for chain propagation k_p. A variety of methods have been used to measure the number of active centers in polymerization with Ziegler catalysts. Here, we used the inhibition method with carbon monoxide for the estimation of the number of active centers during the polymerization. This method was considered most applicable to the catalyst systems, which show nondecaying or very slow decaying in polymerization rate with time. On the assumption that one molecule of CO is adsorbed on each active site, the number of active sites may then be evaluated by extrapolation of the plots of % drop in rate versus amount of CO adsorbed to 100% drop in rate.[5,22] On the addition of a prescribed amount of CO into the reactor through deep-tube
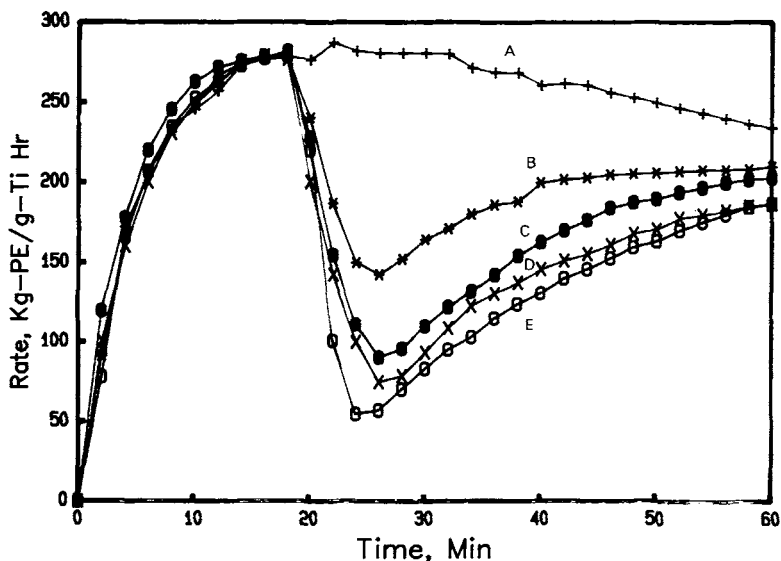

Fig. 13. Effect of CO on the rate of ethylene polymerization. Polymerization conditions: $T = 80°C$; $P = 11.0$ kg/cm^2; [Ti] = 1.785×10^{-5} mol; [AlEt$_3$] = 3.6 mmol/L: (A) [CO]/[Ti] = 0.0; (B) 0.62×10^{-2}; (C) 1.37×10^{-2}; (D) 1.60×10^{-2}; (E) 1.88×10^{-2}.
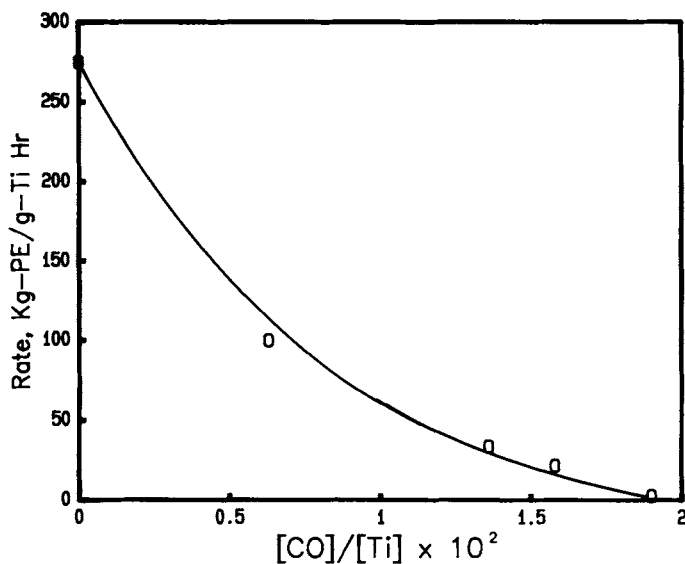
Fig. 14. Decay of polymerization rates by the amount of CO added. Polymerization conditions are the same as in Figure 13.

TABLE IV
The Number of Propagation Center C^* and the Propagation
Rate Constant (k_p) in Ethylene Polymerization

Catalyst system	T (°C)	R_p (kg C_2H_4/g Ti h)	C^* (mol/mol Ti)	$k_p \times 10^{-4}$ (1/mol s)
δ-TiCl$_3$ 0.3 AlCl$_3$[23]	80	2.30	0.001	1.20
TiCl$_4$ + Mg(OR)$_2$[24]	60	57.00	0.020	1.20
TiCl$_4$/MgCl$_2$[25]	80	830.00	0.36	1.20
TiCl$_3$ MgClBr[22]	60	150.00	0.600	0.12
This work	80	280.00	0.019	1.80

feed line, the polymerization rate decreased sharply, then recovered gradually, as shown in Figure 13.

The number of active centers C^* from the minimum amount of CO necessary to stop the polymerization completely was determined as shown in Figure 14, assuming that only one molecule of adsorbate must be adsorbed per active site or else the stoichiometry must be determined.[22] Caunt concluded that the upper limit of C^* could be obtained by the CO inhibition method. Calculated results are shown in Table IV with those from other selected catalyst systems. K_p's were calculated from the relation $R_p = k_p C^*[M]$.

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