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Polymerization of propylene by highly active catalysts synthesized with $Mg(OEt)_2$/benzoyl chloride/$TiCl_4$

Determination of active site concentration by CO inhibition method

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SUMMARY

Active centers have been studied in the polymerization of propylene using highly active $Mg(OEt)_2$/Benzoyl chloride/$TiCl_4$ catalysts activated with $AlEt_3$. The method for the measurement of active centers is based on the inhibiting effect of CO on polymerization. The activity of the present catalysts, which is higher than that of $TiCl_3$ or $MgCl_2$-supported catalyst, is mainly due to the higher concentration of active centers by one order of magnitude. In order to investigate the stability of active centers during polymerization the number of active centers are compared at various polymerization times.

INTRODUCTION

Significant progress in olefin polymerization catalysts has been made in the last 20 years, particularly with the development of methods to increase the efficiency of transition metal catalysts (1). In the previous paper (2) we described a detailed step in preparing highly active and isospecific catalysts based on halogenating a $Mg(OEt)_2$ with $TiCl_4$ containing benzoyl chloride (to generate ethyl benzoate (EB) in situ) in the presence of chlorobenzene, followed by repeated treatments of the resultant solid with $TiCl_4$. Propylene polymerization using a series of catalysts obtained at four different preparation steps showed different rate profiles: two of them were represented by an acceleration-type rate profile and the others a decay-type (2).

In this paper we attempted to determine the number of active centers, C^*, and the value of propagation rate constant, k_p, in order to elucidate the causes of high activity and the interesting kinetic feature of the active centers for the propylene polymerization with a series of catalysts synthesized by $Mg(OEt)_2$ as a starting material.

EXPERIMENTAL

Materials Polymerization grade of propylene (from Korea Petrochem. Co.) and extra pure grade of CO (from Matheson Co.) were used after passing them through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. Extra pure heptane (from Tedia Co., USA) and hexane (from Duksan Pharmaceutical Co., Korea) were dried over Na and fractionally distilled before use. Chlorobenzene (BzCl, from Kanto Chemical Co., Japan) and

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*To whom all correspondence should be addressed benzoyl chloride (BzCOCl, from Kanto Chemical Co.) were purified according to previous method (2). Magnesium diethoxide (from Strem Chem. Co.), $AlEt_3$ (from Aldrich), and $TiCl_4$ (from Kanto Chemical Co.) were used without further purification.

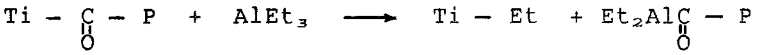
Preparation of Catalysts Catalysts were prepared accoriding to the previous method (2). Magnesium ethoxide (50 mmole) was stirred at room temperature with BzCOCl (15.6 mmole, to generate ethyl benzoate in situ) and 75 ml of BzCl as $TiCl_4$(75 ml) was added over the course of 20 min. The mixture was brought to 100°C for 180 min then filtered hot. The resulting solid was washed at room temperature with seven 150 ml portions of hexane and finally suspended in hexane (called KIPB). The hot-filtered solid from the former step was slurried in 75 ml of BzCl and held at 100°C for 120 min then filtered hot. The brown solid was washed and finally suspended in hexane (called KIPC). Again the filtered solid from the former step was slurried in $TiCl_4$(50 ml) containing BzCOCl (5.2 mmole) and reacted at 100°C for 120 min then filtered hot. The greenish solid was washed then suspended in hexane (called KIPD). Finally the hot-filtered solid from the former step was slurried with $TiCl_4$ (50 ml) and held at 100°C for 120 min. then filtered hot. The green solid was washed then slurried in hexane (called KIPE).

Polymerization The polymerization was carried out in a 250 ml round flask equipped with a stirrer. First, 100 ml of heptane containing prescribed amount of $AlEt_3$ was introduced into the reactor in which the temperature was raised to 50°C, then propylene was saturated to heptane. When no more absorption of propylene by heptane was observed, a prescribed amount of catalyst slurry was added into the heptane solution and then the polymerization was started. The polymerization rate was measured according to the previous method (3). When required, prescribed amounts of carbon monoxide were added during polymerization by means of a gas-tight syringe and a decrease in the overall rate of polymerization was measured simultaneously in order to determine the number of active centers (3, 4).

RESULTS AND DISCUSSION

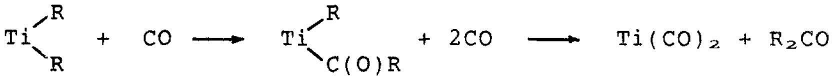
Apart from a scientific interest, the assessment of the active components of a catalyst has a direct bearing on such practical matters as the exploration of the scope for increase in catalyst activity (5). A variety of methods have been used to measure the number of active sites in polymerization with Ziegler-Natta catalysts and assess propagation rates. These have been well reviewed recently (5-7). A stepwise retardation of polymerization using a strong catalyst poison is a procedure characterizing this type of methods (3,8). In essence, the decrease of the polymerization rate is correlated with the consumption of the poison. The amount of poison consumed is determined from a material balance and it is a measure of the number of active centers. Here, we applied an inhibition method using carbon monoxide for the determination of the number of active centers C^* during the propylene polymerization with four different catalysts combined with $AlEt_3$.

By the addition of CO into the gaseous phase of a polymerization a rapid equilibrium of CO between the gaseous and solvent phases and between the solvent phase and catalyst surface takes place (5). Carbon monoxide dissolves in the solvent and is chemisorbed onto the active centers with the result that the rate of polymerization falls sharply to a level which is determined for a given catalyst by the amount of CO added. Typical plots illustrating the phenomena are shown in Fig. 1 for KIPB through KIPE catalysts combined with $AlEt_3$ at different polymerization times. The gradual recovery after sudden decrease of polymerization rate has been interpreted in terms of a slow transfer reaction by $AlEt_3$ for a titanium-acyl bond arising from the insertion of CO into a titanium-polymer bond as shown below (8).



$$Ti - \underset{\overset{\|}{O}}{C} - P + AlEt_3 \longrightarrow Ti - Et + Et_2Al\underset{\overset{\|}{O}}{C} - P$$

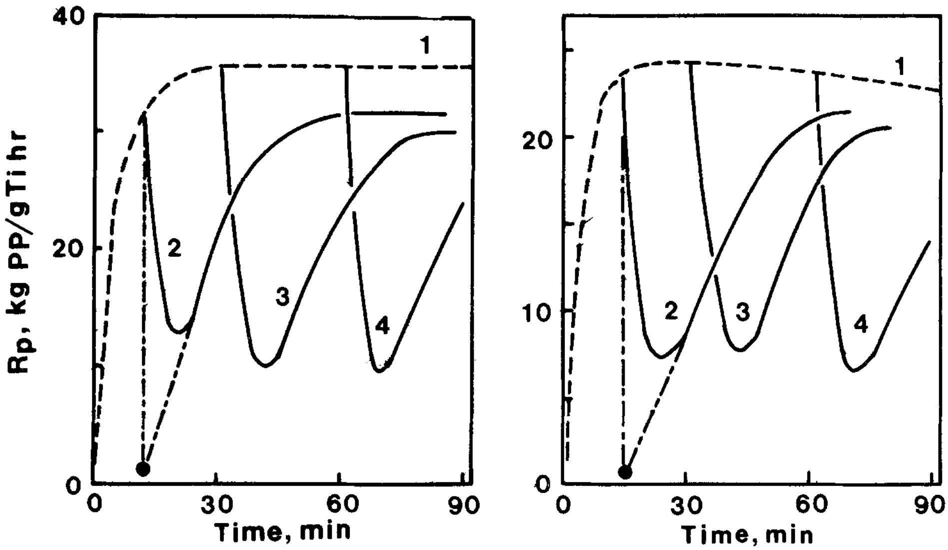
It is interesting to note from Fig. 1 that some 5 to 20 % of the rate is permanently lost. Caunt et al. proposed that the irreversible loss of a proportion of polymerization activity after CO treatment was due to an alternative route to the catalyst regenerating reaction (9). Thus, RTiC(O)R species can be regenerated, whereas $Ti(CO)_2$ species can not.



The reduction in Ti oxidation state occurs in this reaction and the sites are no longer activated.

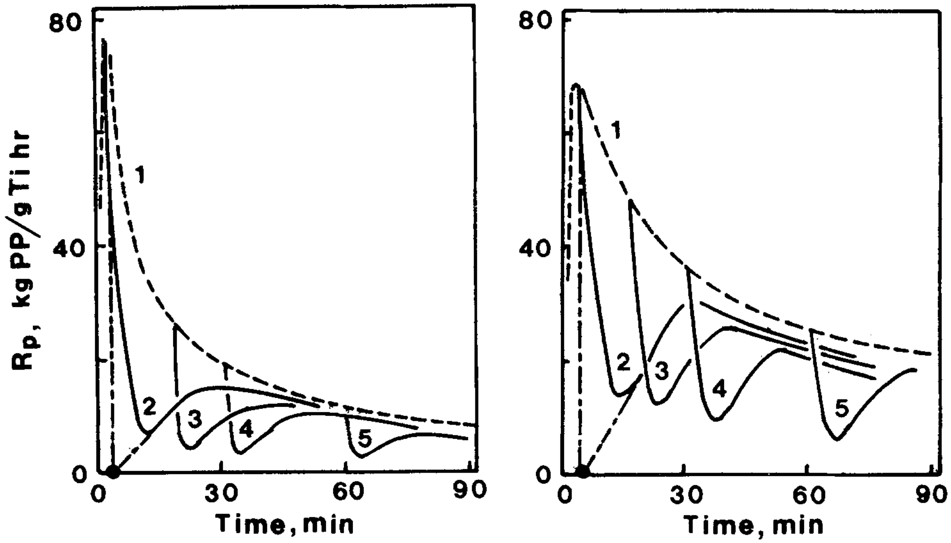
Evaluation of the change of R_p and of the amount of CO consumed was carried out and an appropriate plots are shown in Fig. 2. It can be seen that the overall rate of polymerization is almost constant over a polymerization period of 90 min for KIPB and KIPC catalysts, and therefore the amounts of CO required for zero rate do not change much at 10 min, 30 min, and 60 min of polymerization times. However, the rate of polymerization by KIPD and KIPE catalysts changes drastically as a function of time: the former obeys a second-order decay and the latter a first-order decay (Fig. 1(c) and (d)). It can be seen from Fig. 2(c) and (d) that the amounts of CO required for zero residual polymerization rate also change dramatically with time. On the assumption that one molecule of CO is adsorbed on each active center, the number of active centers may then be evaluated by extrapolation of the plots of % drop in rate versus amount of CO adsorbed to 100 % drop in rate at different polymerization times. The results are summarized in Table 1, together with the rate constant for chain propagation, k_p, calculated from the relation that the overall rate of polymerization, Rp, is given by the simplistic equation, $Rp = k_pC^*[M]$, with the observed values of C^* and the data obtained from references.

As to the methods for the determination of active center concentration based on the assumption that a molecule of CO



(a) KIPB/AlEt$_3$ catalyst:
(1) no CO added, (2) when [CO]/[Ti] = 0.185 at 10 min,
(3) and (4) when [CO]/[Ti] = 0.21 at 30 and 60 min, respectively.

(b) KIPC/AlEt$_3$ catalyst:
(1) no CO added, (2)-(4) when [CO]/[Ti] = 0.168 at 10, 30, and 60 min, respectively.



(c) KIPD/AlEt$_3$ catalyst:
(1) no CO added, (2) when [CO]/[Ti] = 0.258 at 5 min, (3) 0.082 at 15 min, (4) 0.054 at 30 min, (5) 0.035 at 60 min.

(d) KIPE/AlEt$_3$ catalyst:
(1) no CO added, (2) when [CO]/[Ti] = 0.332 at 5 min, (3) 0.21 at 15 min, (4) 0.168 at 30 min, (5) 0.105 at 60 min.

Figure 1. The change in the rate induced by the addition of CO during polymerization. Polymerization conditions: 50°C, [Ti] = 0.41 mg, [M] = 0.43 mol, and Al/Ti = 47.

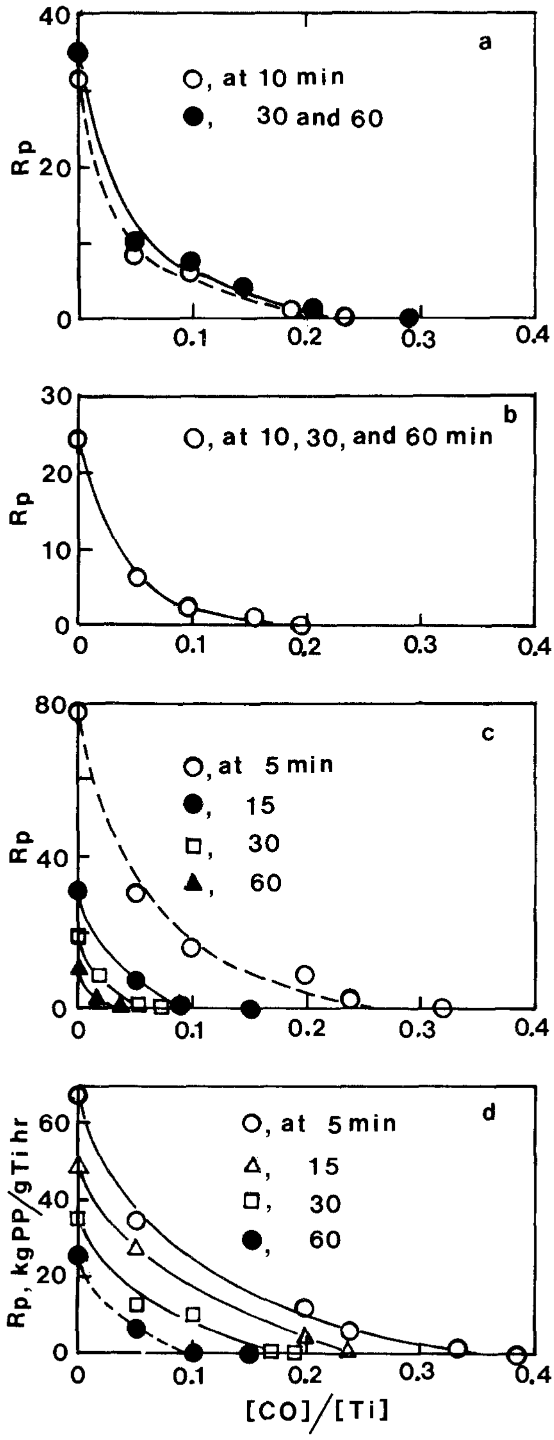


Figure 2. Relation between the polymerization rate and the amount of CO added. Polymerization conditions are the same as those indicated in Fig. 1.
(a) KIPB/AlEt$_3$, (b) KIPC/AlEt$_3$, (c) KIPD/AlEt$_3$, (d) KIPE/AlEt$_3$ catalyst system.

Table 1. The number of active centers, C* , and the average propagating rate constant, k_p, in the propylene polymerization with different catalyst systems.

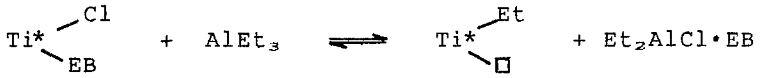
Catalyst system	Temp. (°C)	Time (min)	10^2 C* (mol/mol Ti)	k_p (l/mol s)
$TiCl_4/MgCl_2/EB/AlEt_3$ (10)	38	10	1.6	320
	38	30	1.0	320
	38	60	0.6	360
$TiCl_3/AlEt_2Cl$(10)	41	80	0.8	32
$TiCl_3/AlEt_3$(10)	40	-	1.5	31
KIPB/$AlEt_3$	50	10	19.0	186
	50	30	21.0	184
	50	60	21.0	179
KIPC/$AlEt_3$	50	10		
	50	30	17.0	154
	50	60		
KIPD/$AlEt_3$	50	5	26	332
	50	15	8.4	347
	50	30	5.7	352
	50	60	3.8	324
KIPE/$AlEt_3$	50	5	33	224
	50	15	22	236
	50	30	17	230
	50	60	11	248

reacts with active centers quantitatively, the following remarks should be made. According to this method, small amounts of CO result in a nearly instantaneous decrease of polymerization activity due to the high affinity of CO for active centers. If reduced polymerization rate is plotted vs. the amount of CO, complete catalyst deactivation will be noted when the amount of CO added is equal to the number of polymerization centers. However, CO can, in principle, adsorb on some other species on the catalyst surface in addition to the polymerization centers (9). Thus, the method provides information about the lowest possible concentration of active centers.

The results show that the number of active center of KIPB through KIPE catalysts is higher than that of $TiCl_3$ and $TiCl_4/MgCl_2/EB/AlEt_3$ by one order of magnitude, and that the values of k_p of the KIPB through KIPE are of the same order with that of the magnesium chloride-supported catalyst and are higher than that of $TiCl_3$ by one order of magnitude. Accordingly the superior activity of the present catalyst systems over that of magnesium chloride-supported catalyst or $TiCl_3$ is due to the higher value of k_p as well as to the higher concentration of active center. When comparing values of C* for different catalyst systems it is important to state the appropriate time of determination. This is of considerable importance when dealing with a catalyst system of the Montedison-Mitsui type, e.g. $MgCl_2/TiCl_4/EB$, in which the rate of polymerization can change sharply as a function of time. As shown in Table 1, the decrease of the C* value during polymerization with $MgCl_2$-supported catalyst is second order with respect to the polymerization time and the k_p value is almost constant throughout the decay of C* .

A similar change in C* value and k_p value with time was observed for KIPD/$AlEt_3$ catalyst system in spite of the higher C* value by an order of magnitude than $MgCl_2$/EB/$TiCl_4$/$AlEt_3$ catalyst. The magnitude of C* decreased following the second order decay with respect to polymerization time and k_p values do not change much during polymerization. The C* value of KIPE/$AlEt_3$ catalyst system changes also during polymerization to a lesser degree than KIPD/$AlEt_3$ and the k_p values are almost constant as in the case of KIPD/$AlEt_3$ between 224 and 248 l/mol sec. However, both C* and k_p values do not change much during polymerization with KIPB/$AlEt_3$ and KIPC/$AlEt_3$ catalyst systems.

For KIPD and KIPE catalyst, the interaction between EB and Ti species and/or $MgCl_2$ is not so strong that some of EB can be removed from the catalyst surface by forming a complex with $AlEt_3$ in the following manner (2),



where EB is ethyl benzoate, and □ represent a vacant coordination site. The resulting Lewis acidic Ti unsaturated sites can polymerize ethylene, but in the case of propylene these sites either produce stereo-irregular polymers or are inactive. The second order decay of active sites, C* , also indicates the dimerization of this unsaturated species into the inactive species. On the other hand the interaction between EB and catalytic active species is so strong for KIPB and KIPC catalyst that the dissociation might be retarded or not occur. Accordingly, when polymerization is carried out with the KIPD and KIPE catalyst, the number of donor-free active species which interact with the neighboring donor-free active species to be deactivated according to the second- or first-order kinetics markedly increases with polymerization time. The novel stability of active centers of KIPB and KIPC is mainly attributed to the strong interaction between EB and $AlEt_3$. The evidence for strong interaction of EB with catalytic active species in KIPB and KIPC were obtained from the IR and extraction experiment with $AlEt_3$ which is described else-where in detail (2).

REFERENCES

1. F. J. Karol, Catal. Rev. -Sci. Eng., 26, 557 (1984).
2. I. Kim and S. I. Woo, Makromol. Chem., submitted (1989).
3. I. Kim, J. H. Kim, and S. I. Woo, J. Appl. Polym. Sci., in press
4. A. D. Caunt, Br. Polym. J., 13, 22 (1981).
5. P. J. T. Tait, "Transition Metal Catalyzed Polymerization", MMI Press Symposium, Harwood Academic Publisher: 1983, P. 115.
6. J. Mejzlik, P. Vozka, J. Kratochvila, and M. Lesna, "Transition Metals and Organometallics as catalyst for

Olefin Polymerization", Springer-Verlag, 1988, p.79.
7. A. D. Caunt, Catalysis (London) 1, 234 (1977).
8. J. Kratochvila and J. Mejzlik, Makromol. Chem., 188, 1781 (1987)
9. A. D. Caunt, S. Davies, and P. J. T. Tait, "Transition Metal Catalyzed Polymerizations", Akron Symposium, Cambridge Univ. Press, 1988, p. 105.
10. T. Keii, E. Suzuki, M. Tamura, M. Murata, and Y. Doi, Makromol. Chem., 185, 2285 (1982).

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