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Homo- and co-polymerization of ethylene with highly active Ti/Mg bimetallic complexes

Effect of crystallization conditions on structure and productivity

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SUMMARY

Homo- and co-polymerization of ethylene were performed by using a catalyst system composed of recrystallized $MgCl_2$ $TiCl_4$ THF complex with $AlEt_3$. The effect of crystallization conditions during the catalyst preparation on the chemical composition and physical structure of catalysts was discussed with the help of element analysis, IR spectroscopy, and X-ray powder diffraction. The variation caused by different crystallization conditions had considerable influences on the rate profiles of homo-and co-polymerization of ethylene.

INTRODUCTION

Recently a novel technique for the preparation of supported catalysts for ethylene polymerization was invented. It consists of dissolution of anhydrous $MgCl_2$ and $TiCl_4$ in an electron donor solvent, followed by co-crystallization of the catalytically active ingredients and the supports from the solutions (1-3). Unlike surface complexes formed by chemical anchoring to a substrate, such complexes have been reported to have unique X-ray diffraction patterns (4). For this type of catalystic system, the chemical and physical state of catalyst has a significant influence on the activity and rate behavior of polymerization. In some cases excess Mg and/or Ti compound may not participate in the preparation of Mg/Ti complexes depending on crystallization conditions. Accordingly, crystallization conditions are one of the important factors to be considered for the preparation of crystallized catalysts. However, there have been no published results on this subject.

In the present study, we prepared Mg/Ti bimetallic catalysts of different chemical composition and physical structure by changing the crystallization conditions. The activity and polymerization rate profiles of these bimetallic complexes were evaluated in the homo-and copolymerization of ethylene.

EXPERIMENTAL

Materials; Polymerization grade of ethylene (Yukong Ltd., Korea) and nitrogen of extra pure grade were further purified with the columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. 1-Hexene (Aldrich, USA) was passed through molecular sieve 5A and 13X. n-Hexane of extra pure grade (Duksan, Ltd., Korea) was dried by refluxing over sodium metal in a nitrogen atmosphere, and passed through the columns of $CaSO_4$ and molecular seive 5A. 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.

Catalysts preparation; In a 1 l round bottom flask equipped with a magnetic stirrer, condenser, and inlet tube for N_2, 60 mmole of $MgCl_2$ was mixed with 400 ml of pure THF under nitrogen. The temperature of the reaction mixture was subsequently increased to the boiling point of THF with a vigorous stirring. After this solvated complex was cooled to room temperature, 20 mmole of $TiCl_4$ was added dropwise for 15 min. Upon complete addition, the contents of the flask was refluxed for 2 hours while stirring. This solvated bimetallic complex was divided into 4 parts. Each part of solution was crystallized to obtain a yellow solid complex at 60°C, 25°C, 0°C, and -10°C, by adding 300 ml of dry n-hexane slowly over a period of 15 min. The supernatent liquid was decanted, then the yellow complex was washed with 100 ml of n-hexane three times to remove uncomplexed $TiCl_4$ and $MgCl_2$. These solid complexes were dried at room temperature in vacuum and stored under inert atmosphere. These complexes do not have coordinatively unsaturated sites because of the presence of strong electron donor, THF. The complex cryatallized at 25°C was washed with excess amount of $AlEt_3$ (Al/Ti = 5) to remove THF from the complex in order to compare the polymerization kinetics with that of catalyst unreacted with $AlEt_3$ before polymerization.

Polymerization; Slurry polymerization was performed in a 1 l autoclave under a constant pressure of ethylene. A prescribed amount of $AlEt_3$ and 500 ml of n-hexane were introduced into the reactor in a nitrogen stream. 1-Hexene was also introduced in the case of copolymerization. After evacuation, ethylene was introduced at the polymerization temperature. Polymerization was started by breaking the glass ampoule containing the prescribed amount of catalyst. The rate of polymerization was determined from the rate of ethylene consumption, measured by a hot-wire flowmeter with a personal computer directly connected to it through A/D converter. Details of polymerization procedures have been previously described (5).

Analyses; The content of titanium was determined photometrically. Mg was evaluated through atomic absorption spectroscopy (Allied Analytical Systems). Chlorine was determined by back titration according to Volhard's method (6). The amount of THF was measured by hydrolysis-GC methods (3). FTIR spectra were recorded with a instrument with 25 mm NaCl window using a mull techniques. X-ray analysis was carried out in a special cell with a poly(ethylene terephtalate) film window on a Rigaku Geigerflex 2013 diffractometer with a monochromatic copper radiation. The morphology of catalysts was examined using electron microscope techniques at inert atmosphere. The melting points of polymers were determined from the peaks of DSC curves obtained with a Perkin Elmer DSC-4. Sample weights and scan rate were about 4-6 mg and 10° C/min, respectively.

Table 1. Chemical compositions of various complexes crystallized at different temperatures.

Complex	Mg wt%	Ti wt%	Cl wt%	THF wt%	Cryst. temp. (°C)	Mg/Ti
KI00	9.58	-	33.58	56.84	25	-
KI01	10.00	1.67	32.62	55.71	60	11.87
KI02	8.53	3.20	34.74	53.52	25	5.27
KI03	7.67	3.60	35.00	53.73	0	4.19
KI04	5.80	3.73	33.15	57.32	-10	3.06
KI05[a]	14.30	9.19	76.50	trace	25	5.27

a: KI05 was prepared by washing KI02 with excess $AlEt_3$

RESULTS AND DISCUSSION

Element analysis of Ti/Mg bimetallic complexes; Table 1 shows the results of element analysis of bimetallic complex catalysts cocrystallized at different temperatures. The mole ratio of Mg to Ti in the precursor solution is 3 regardless of crystallizaton temperature. However, the final compositions of Mg and Ti were deviated significantly from this ratio. This is due to the differences in the solubility of $MgCl_2$ THF and $TiCl_4$ THF complexes to THF and n-hexane at different crystallization temperatures. At the higher crystallization temperature, the solubility of $TiCl_4$ THF complex was smaller than that of $MgCl_2$ THF complex and vice versa. Accordingly Mg/Ti ratio in the bimetallic complex becomes smaller as the crystallization temperature decreases.

IR study; In order to characterize the complexes shown in Table 1 and to determine the extent of complexation key absorptions in the infrared were monitored (Table 2). The IR spectrum of neat THF is characterized by a symmetrical C-O-C stretching vibration at 910 cm^{-1} and an asymmetrical C-O-C stretching vibration at 1071 cm^{-1}. These C-O-C bands of THF shifted to 1038 cm^{-1} and 890 cm^{-1} by reaction with $MgCl_2$ due to the complexation between $MgCl_2$ and THF. Due to a strong Lewis acidity $TiCl_4$ forms stronger complexation with THF than $MgCl_2$. This can be identified by comparing the degree the C-O-C bands were shifted to lower frequencies. The shift in the symmetrical C-O-C band is $\Delta\nu = -85\ cm^{-1}$ for $TiCl_4\ (THF)_{2.0}$ complex and is $\Delta\nu = -20\ cm_{-1}$ for $MgCl_{2.4}\ (THF)_{2.0}$ complex. The shift in the asymmetrical C-O-C band is $\Delta\nu = -77\ cm^{-1}$ for $TiCl_4\ (THF)_{2.0}$ complex and is $\Delta\nu = 33\ cm^{-1}$ for $MgCl_{2.4}$ $(THF)_{2.0}$ complex. For $MgCl_2$-$TiCl_4$-THF complex the extent of the shift to lower frequencies in the two C-O-C bands was different according to Mg/Ti ratio. As the Mg/Ti ratio of the catalyst increased, the extent of shift became large (Table 2). This may be caused by the dilution of $[TiCl_5(THF)]^-$ anion with strong complexation by the $MgCl_2$ THF complex matrix. The $[TiCl_5\ (THF)]^-$ anion was produced in the reaction between $TiCl_4$ THF complex and $MgCl_2$ THF complex by removing the chlorine atoms from $MgCl_2$ THF complex by titanium atom due to the strong acid property of titanium atom. The titanium atom in the $[TiCl_5\ (THF)]^-$ anion is pseudo-octahedrally coordinated with shorter axial than equatorial Ti-Cl bonds (7-9). The Ti

Table 2. Infrared data on magnesium-titanium-THF compositions.

Diagnostic infrared absorbances (cm^{-1})	
THF	1071, 910
$MgCl_{2.4}(THF)_{2.0}$ (KI00)	1038, 919, 890
$TiCl_4\ (THF)_{2.0}$	994, 825
$TiMg_{11.87}Cl_{26.54}(THF)_{22.29}$ (KI01)	1034, 919, 885
$TiMg_{5.24}Cl_{14.60}(THF)_{11.07}$ (KI02)	1027, 920, 874
$TiMg_{4.19}Cl_{13.11}(THF)_{9,89}$ (KI03)	1027, 920, 873
$TiMg_{3.06}Cl_{11.99}(THF)_{10.19}$ (KI04)	1026, 921, 872

anions are diluted Mg complex solid matrix when the Mg/Ti ratio of the complex is high so that the complexes with higher Mg/Ti ratio shift to a less degree. New absorption appearing about 920 cm^{-1} for all catalysts may be related with the interaction of $MgCl_2$ with THF. This band was not observed for $TiCl_4\ (THF)_2$ complex.

X-ray diffraction study; Upon crystallization of solvated $MgCl_2$ THF complex, the typical diffraction pattern of anhtdrous $MgCl_2$ disappeared due to the formation of new complex, $MgCl_{2.4}\ (THF)_2$ (Table 3). In addition, most reflections of $MgCl_2$ THF complex were considerably broadened in comparison with those of anhydrous $MgCl_2$. It indicates that the crystallite size of $MgCl_2$ becomes significantly redcuced by the complexation of $MgCl_2$ with THF. The $MgCl_2$, as received, shows strong reflections at $2\theta = 15.3°$, $30.4°$, $35.2°$, $46.3°$, and $50.4°$. The strong reflection at d = 2.56 A (35.2°) displays that the anhydous $MgCl_2$ is cubic close packed (ccp) structure, which is similar in structure to γ-$TiCl_3$, with ABCABC---- stacking sequence (10). However, the most intense reflection in $MgCl_{2.4}\ (THF)_{2.0}$ complex is found at d = 2.78 Å (32.5°). This is consistent with the presence of more hexagonal close packed (hcp) structure which is similar to α-$TiCl_3$, with ABAB---- stacking sequence than ccp structure. The 2θ reflections of $MgCl_{2.4}\ (THF)_{2.0}$ at 38.4°, 39.3°, and those between 15.4° and 22.1° have not been noted in the previous reports. They may arise from the rotationally disordered structure. The catalysts prepared by the cocrystallization of solvated complex of $TiCl_4$, THF, and $MgCl_2$ at various crystallization temperatures shows their characteristic x-ray diffraction patterns according to Mg/Ti ratios as shown in Table 3. KI01 catalyst with highly excess Mg/Ti ratio, 11.87, displays similar x-ray diffraction pattern with $MgCl_2$ THF complex. However, catalysts with intermediate Mg/Ti ratio, KI02, KI03, and KI04 catalyst, showed much difference in 2θ reflections from KI01 or $MgCl_2$ THF complex. The strong 2θ reflections of KI02, KI03, and KI04 catalyst were appeared at 11.0°, 17.9 °, 27.9°, and 33.7°. This 2θ reflections have not been noted in the previous reports. The difference of 2θ reflections might be come from the distribution of Mg cation to from ioinic complex with $[TiCl_5\ (THF)]^-$ anion. According to the previous reports (7-9), the Mg cation may be monomeric, $[Mg(THF)_6]^{2+}$, or dimeric, $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$, complex.

Table 3. 2θ angles of the reflection maxima of $MgCl_2$, its reaction product with THF, and catalysts.

$MgCl_2$	KI00	KI01	KI02	KI03	KI04
		2θ values (degree)			
	10.4	11.0	11.0	11.0	11.0
			12.2		12.2
			12.6	12.6	12.6
15.0(a)	15.4	15.0	15.0	15.0	15.0
	16.7	16.7		16.7	
	17.9	17.9	17.9	17.9	17.9
	20.0	20.0	20.0		20.0
	21.0	21.0	21.0		21.0
	22.1	22.1	22.1	22.1	22.1
			23.2	23.2	23.2
30.4			27.9	27.9	27.9
	32.5	32.5	32.5	32.5	32.5
35.2			33.7	33.7	33.7
	38.4	38.4	38.4	38.4	38.4
	39.3	39.3	39.3	39.3	39.3
46.3		48.3			
50.4					
50.6					

(a) underlined angles are five strong reflections.

At high Mg/Ti ratio above 2 dimeric Mg cationic complex is a main compound to form ionic complex with $[TiCl_5(THF)]^-$ anion due to the stoichiometry of Mg/Ti. Thus it may be concluded that the catalysts in the present study are composed of following reactions products.

$$MgCl_2 + 2(THF) \longrightarrow MgCl_2(THF)_2 \qquad (1)$$

$$TiCl_4 + 2(THF) \longrightarrow TiCl_4(THF)_2 \qquad (2)$$

$$2MgCl_2(THF)_2 + TiCl_4(THF)_2 \longrightarrow [Mg_2(\mu\text{-}Cl)_3(THF)_6]^+[TiCl_5(THF)]^- \qquad (3)$$

At highly excess of Mg/Ti ratio, the ionic complex from eq.(3) is diluted in the $MgCl_2(THF)_2$ solid matrix in a manner that ionic complex does not affect on the diffraction pattern of $MgCl_2(THF)_2$ complex. Accordingly, the 2θ reflections of KI01 catalyst (Mg/Ti = 11.87) become similar to those of $MgCl_2(THF)_2$. However, x-ray diffraction patterns of KI02, KI03, and KI04 catalysts with intermediate Mg/Ti ratios are influenced by the ionic complex from Eq. (3) because the proportion of this complex is relatively large in the solid matrix of the catalysts. The strong 2θ reflections of KI02, KI03, and KI04 catalysts appeared at 27.9° and 33.7° which are not observed at KI01 catalyst or $MgCl_2$ THF complex may be caused by the ionic complex in solid matrix existed in relatively large proportion. The particle size of the catalyst was also changed according to the Mg/Ti ratio caused by the different crystallization temperatures. The particles of KI01 catalyst with the highest Mg/Ti ratio were uniform and small in size (sizes up to 50 - 100 μm) due to heterogeneity, while the KI04 catalyst with lowest Mg/Ti ratio was irregular and large in size (sizes up to 10 - 350 μm). Details of the inner morphology of the catalysts could be observed at high magnification using SEM micrographs. KI01 catalyst was build-up (secondary particle, about 0.4µm in diameter and 1.8 fm in length) by agglomeration of subparticles (primary particles) having disc shape (about 0.4µm in diameter). KI04 catalyst was similar to KI01 catalyst in shape and structure. However, the diameter and length of secondary particles of KI04 catalyst were larger than those of secondary particles of KI01 catalyst by about 3 times, even if the primary particles remain almost same in size. Generally, the size of secondary particles increased as Mg/Ti ratio of the catalyst decreased. However, there was no significant difference in the size of primary particles regardless of Mg/Ti ratio.

Homo-and co-polymerization of ethylene; Each catalyst prepared at different crystallization temperatures shows a characteristic kinetic profile in homopolymerization of ethylene and copolymerization of ethylene with 1-hexene. The profiles in the homopolymerization of ethylene are shown in Fig. 1. The activity of catalyst decreases as the Mg/Ti ratio of catalysts decreases. In addition, all catalysts have considerable induction times, as it were, the polymerization rates reach maximum after 15 - 30 min. The shorter the induction times, the larger the Mg/Ti ratio of catalyst is. This result may be come from the difference of activation process of Ti surface sites distributed onto Mg complex solid matrix. Catalysts of lower Mg/Ti ratios are in the form of larger crystals due to incomplete heterogenity as discussed in previous section. Therefore, they needed longer time to be grinded to primary particles from which polymer chains grow during the early polymerization period. The rate profile of the catalyst washed with the solution of excess $AlEt_3$ (KI05) is different from that of the catalyst not washed with $AlEt_3$ (see Fig. 1 (b) and (e)). The former was already partially activated with $AlEt_3$, resulting in the shorter time to reach the maximum rate. However, the average polymerization rate increased slightly. This indicate that THF was removed by the reaction with $AlEt_3$ during the initial stage of polymerization. Hence, the rate profile after the prolonged time of polymerization will be same whether THF is removed before polymerization or not.

The increase of activity of the catalysts with the increase of Mg/Ti ratio is related with the utilization of Ti centers. In the present catalyst system, octahedrally coordinated Ti anions are diluted by Mg ions by entering the crystalline matrix of complex salt as discussed in previous section. Therefore, the distribution effect of Ti anions influences the number of active centers. As the Mg/Ti ratio of the catalyst increases, the Ti anions are more evenly distributed onto catalyst surface in the form of isolated, octahedrally coordinated ions. This indicates that an excess of Mg compound with respect to Ti compound implies usually the heterogeneity of the catalyst (4). The distribution effect of Ti anions can be estimated by comparing Fig. 1 and Fig. 2, in which the rate of polymerization is normalized to kg PE/g-Ti hr. The difference of productivity based on the gram of catalyst (Fig. 2) was not significant in comparison with the difference of productivity based on the Ti atom of catalyst (Fig.

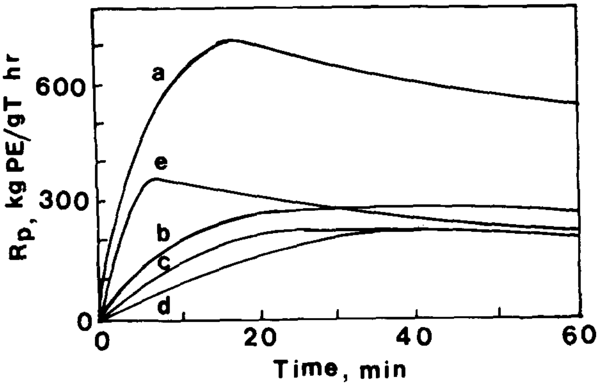

Fig. 1. Ethylene polymerization at 70°C, ethylene pressure = 3.0 atm, and Al/Ti = 128 by (a) KI01 catalyst, (b) KI02, (c) KI03, (d) KI04 and (e) KI05. $AlEt_3$ was used as cocatalyst.

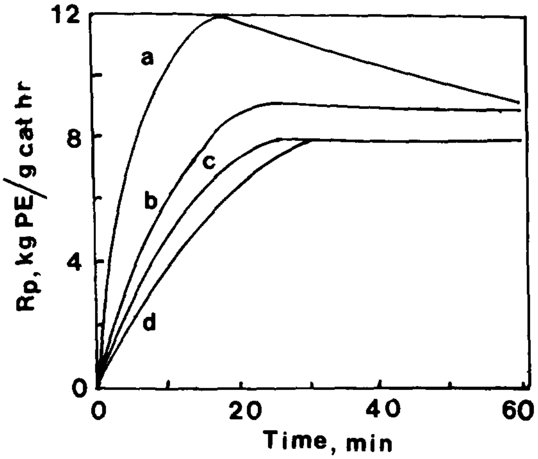

Fig. 2. Polymerization rate profiles normalized to the gram of catalyst. Polymerization conditions and captions are same as those in Fig. 1.

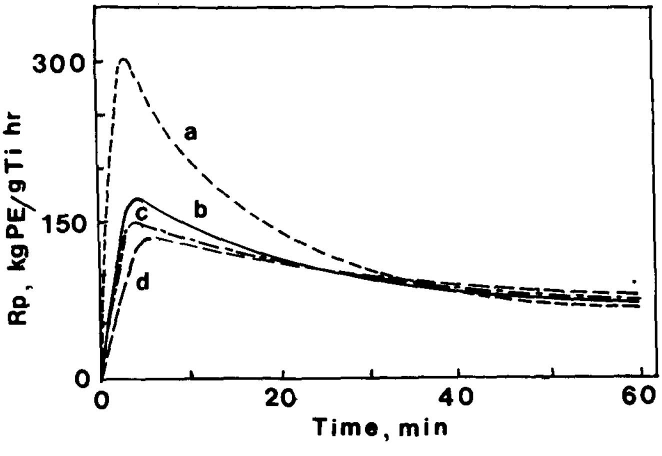

Fig. 3. Ethylene copolymerization with 1-hexene: T = 70°C, ethylene pressure = 2.0 atm, [1-hexene] = 0.24 mol/l, and Al/Ti = 128 by (a) KI01 catalyst, (b) KI02, (c) KI03, and (d) KI04. $AlEt_3$ was used as a cocatalyst.

1). It may be concluded from this result that Ti anions can be utilized more effectively as the Mg/Ti ratio of catalyst increases.

Fig. 3 show the kinetic profiles of ethylene copolymerization with 1-hexene. No significant induction times were appeared by the addition of 1-hexene. This indicates that 1-hexene in reaction medium accelerates the initial activation of catalyst surface sites by the formation of new active centers due to the coordination of 1-hexene to the initial active centers. After reaching maximum quickly, the polymerization rates starts to decay. The decay rate increases as the Mg/Ti ratio increases at the same concentration of 1-hexene. Therefore, average copolymerization rates over an hour do not show large difference as in the case of homopolymerization. The percentage of crystallinity of homopolymer (71 %) determined by heat of fusion decreased considerably by the incorporation of 1-hexene. The crystallinity of copolymers produced by KI02, KI03, and KI04 catalysts with intermediate Mg/Ti ratios showed similar crystallinities (53 -54 %), but copolymer by KI01 catalyst in excess Mg/Ti ratio (11.87), had much lower crystallinity (50.3 %). From above results, it can be confirmed that reactivity of 1-hexene is high at excess Mg/Ti ratio.

References

1. US 4124532 to Montedison S. p. A., 1978.
2. US 4481301 to Mobil Oil Co., 1984.
3. US 4302565 to Union Carbide Co., 1981.
4. A. Greco, G. Bertollini, and S. C. Assoreni, J. Appl. Polym. Sci. 25, 2045 (1980).
5. I. Kim, J. H. Kim, and S. I. Woo, in press, J. Appl. Polym. Sci.
6. D. A. Skoog and D. M. West, " Analytical Chemistry ", Saunders College, Philadelphia, 1980, pp 581.
7. P. Sobota and J. Utko, Polym. Comm., 29, 144, 1988.
8. P. Sobota, J. Utko, and T. Lis, J. Chem. Soc. Dalton Trans. 2077 (1984).
9. P. Sobota, J. Utko, and Z. Janas, J. Organomet. Chem. 316, 19, 1986.
10. N. Kashiwa and A. Toyota, Polym. Bull., 11, 471, 1984.

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