Temperature-Programmed Decomposition of a $MgCl_2/THF/TiCl_4$ Bimetallic Complex Catalyst and Its Effect on Ethylene Polymerization Rate

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ABSTRACT: A $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst was prepared by reacting magnesium chloride with titanium tetrachloride in tetrahydrofuran, followed by precipitation with excess *n*-hexane. The products formed during the thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst were THF and 1,4-dichlorobutane as identified by MS, FTIR, and ^{13}C NMR. The amount of 1,4-dichlorobutane formed during thermal treatment decreased with an increase of the Mg/Ti ratio. It was suggested that some of THF coordinated to Ti reacted with adjacent Cl to form 1,4-dichlorobutane. Ethylene polymerization was performed at 70 °C with bimetallic complex catalysts thermally pretreated at various temperatures. When the temperature of the thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) was below 108 °C, the catalytic activity increased, while the activity decreased above 140 °C. However, the catalytic activity of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 16.5) heated above 80 °C decreased. This indicated that the thermal stability of the catalyst decreased with an increase of the Mg/Ti ratio.

Introduction

The bimetallic complex catalyst prepared by the reaction of magnesium chloride with titanium tetrachloride in tetrahydrofuran (THF) shows high catalytic activity in ethylene polymerization when combined with an aluminum alkyl cocatalyst.[1-4] In this catalyst system $MgCl_2$ plays an important role in dispersing and stabilizing catalytically active Ti species by the formation of discrete chemical complexes between $MgCl_2$ and $TiCl_4$.[2] Reaction between $MgCl_2(THF)_2$ and $TiCl_4(THF)_2$ in THF yields three different bimetallic complexes depending on the molar ratio of Mg to Ti in the complex.[5-7]

When the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst is heated, some of the weakly coordinated THF is removed. The changes in the structure of the catalyst after thermal treatment will affect the catalytic activity of polymerization. The site and strength of coordination of THF to $TiCl_4$ and $MgCl_2$ will affect the catalyst performance. Temperature-programmed decomposition (TPD) of THF from the complex may provide some information which leads to the understanding of the structure of active species in ethylene polymerization. Hence, TPD study of $MgCl_2/THF/TiCl_4$ bimetallic complexes having various molar ratios of Mg to Ti was performed. The decomposed gaseous products during TPD were collected and analyzed with gas chromatography, FTIR, MS, and ^{13}C NMR. The effect of temperature and duration of thermal treatment on the ethylene polymerization rate was also investigated. The change in the coordination of THF after thermal treatment was followed with FTIR measurements.

Experimental Section

The polymerization grades of ethylene (Yukong Ltd., Korea) and nitrogen of extra pure grade were further purified with the columns of Fisher RIDOX and molecular sieve 5A/13X. *n*-Hexane (Duksan Ltd., Korea) of extra pure grade was further purified by refluxing over sodium metal in a nitrogen atmosphere. The analytic grade of tetrahydrofuran (J. T. Baker Chemical Co., Phillipsburg, NJ) was purified by refluxing with $LiAlH_4$ for several hours. Anhydrous magnesium chloride (Aldrich), aluminum trialkyl (Aldrich), and $TiCl_4$ (Kanto Chemical Co., Japan) were used without further purification. The $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst was prepared by the reaction of magnesium chloride with titanium tetrachloride in tetrahydrofuran, followed by precipitation with excess *n*-hexane. Slurry polymerization was carried out in a 1-L autoclave under a constant pressure of ethylene. The detailed procedures for catalyst synthesis and polymerization were described elsewhere.[2,3] The TPD experiment was conducted under a nitrogen flow at a heating rate of 10 °C/min. The temperature was raised from room temperature to 300 °C. When the complexes were thermally decomposed, the amounts of the product gases formed during TPD were monitored by gas chromatography. The gases evolved during TPD of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst were identified by mass spectroscopy, FTIR, and ^{13}C NMR. Mass spectra were obtained with a VG SX300 quadrupole spectrometer during TPD of the catalysts under a nitrogen flow at a heating rate of 10 °C/min. The heating temperature was raised from room temperature to 300 °C. The FTIR spectrum of a liquid sample collected at -196 °C during TPD of the catalyst (Mg/Ti = 5.2) was obtained with FTIR (Bomem MB-102). FTIR spectra of the thermally treated catalysts were recorded on an instrument with a 25-mm NaCl window using a mull technique. The sample for ^{13}C NMR was prepared by condensing the gaseous products in $CDCl_3$ at -196 °C formed during TPD of the catalyst (Mg/Ti = 5.2). This sample was heated at 70 °C to evaporate THF. Tetramethylsilane (TMS) was used as an internal reference. The ^{13}C-NMR spectrum was recorded on a Varian FT-80A spectrometer operating at 20 MHz with proton noise decoupling in Fourier transform mode at 25 °C.

Results and Discussion

In Figure 1 is shown the TPD spectrum of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) monitored by GC. The catalyst was decomposed at 108, 140, and 242 °C. The MS, FTIR, and ^{13}C-NMR experiments were conducted to identify the products formed during thermal decomposition as shown in Figures 2-4.

Figure 2 shows the mass spectra of the gaseous products formed during thermal decomposition of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 80 and 210 °C, respectively. The mass-to-charge ratios (*m/e*) and intensities of THF and 1,4-dichlorobutane in the cracking pattern are shown in Table I.[8] When the catalyst was thermally decomposed at 80 °C, the peak of mass-to-charge

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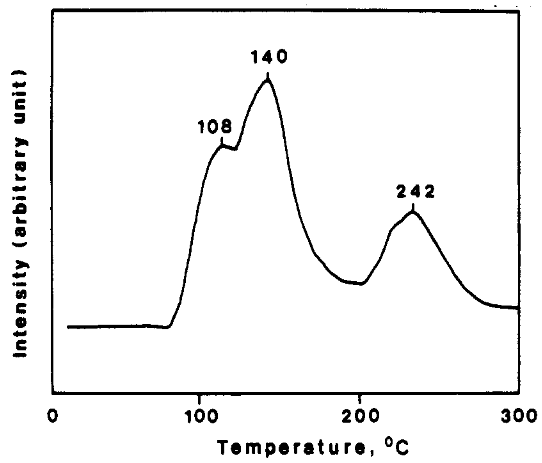


Figure 1. Temperature-programmed decomposition spectrum of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2). Experimental conditions: heating rate = 10 °C/min; N_2 flow rate = 45 cm^3/min; catalyst weight = 0.5 g.

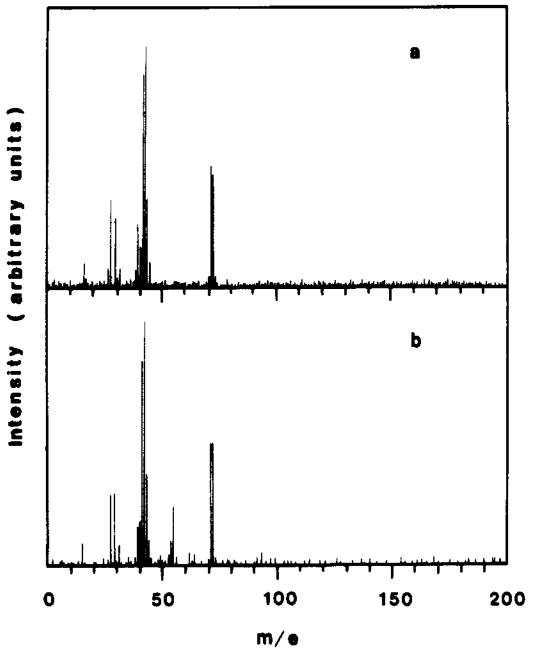


Figure 2. Mass spectra of the gaseous products formed during thermal decomposition of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 80 (a) and 210 °C (b).

Table I
Mass-to-Charge Ratios (*m/e*) and Intensities of THF and 1,4-Dichlorobutane in the Cracking Pattern[8]

	THF	1,4-dichlorobutane
intensities	100, 52, 33, 29, 27, 25, 22, 22	100, 42, 41, 21, 19, 18, 18, 14
mass-to-charge ratios (*m/e*)	42, 41, 27, 72, 71, 39, 29, 43	55, 27, 41, 90, 54, 62, 28, 49

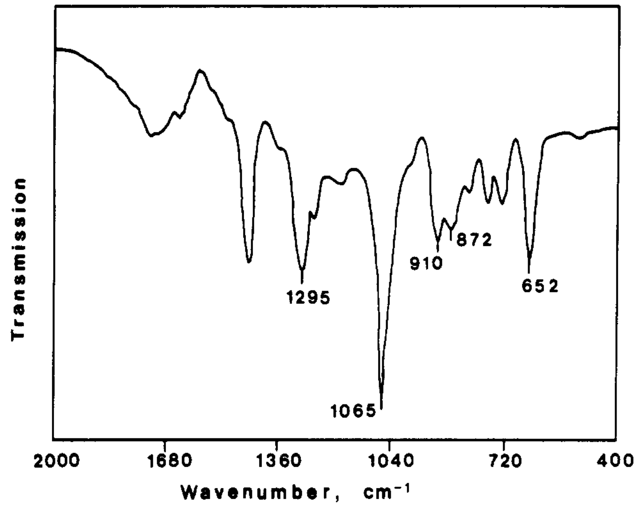


Figure 3. FTIR spectrum of the liquid sample obtained by condensing the gaseous products at −196 °C formed during thermal decomposition of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 210 °C.

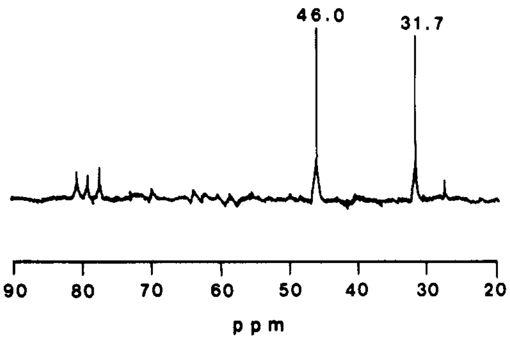
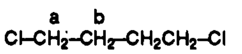


Figure 4. ^{13}C-NMR spectrum of the liquid sample prepared by condensing the gaseous products in a $CDCl_3$ solution at −196 °C formed during thermal decomposition of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 210 °C.

ratio of 55 which was later assigned to 1,4-dichlorobutane was not observed and the peak of mass-to-charge ratio of 42 which was assigned to THF was observed. When the catalyst was decomposed at 210 °C, the peaks of THF and 1,4-dichlorobutane were observed.

Figure 3 shows the FTIR spectrum of the liquid sample obtained by condensing the gaseous products at −196 °C formed during the thermal decomposition of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 210 °C. The band at 652 cm^{-1} is assigned to the C–Cl stretching band and the band at 1295 cm^{-1} to the CH_2 wagging band of CH_2–Cl.[10] The band at 1065 cm^{-1} is assigned to the asymmetrical C–O–C band of THF, and the bands at 910 and 872 cm^{-1} are assigned to the symmetrical C–O–C bands of THF.[2,9]

In Figure 4 is shown the ^{13}C-NMR spectrum of the liquid sample. This liquid sample was prepared by condensing the gaseous products in a $CDCl_3$ solution formed during thermal decomposition of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 210 °C. THF was distilled off at 70 °C. In this spectrum three weak peaks appear around 80 ppm and two strong peaks appear at 31.7 and 46.0 ppm. Three small peaks around 80 ppm are ascribed to $CDCl_3$.[11,12] The peaks of 31.7 and 46.0 ppm are arising from carbon a and carbon b of 1,4-dichlorobutane, respectively.[13]


$$Cl\text{–}\overset{a}{C}H_2\text{–}\overset{b}{C}H_2\text{–}CH_2CH_2\text{–}Cl$$

From the results of mass spectroscopy, FTIR, and ^{13}C NMR it can be concluded that THF and 1,4-dichlorobutane are produced during thermal decomposition of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 210 °C.

In Figure 5 are shown the TPD spectra of $MgCl_2/THF/TiCl_4$ bimetallic complex catalysts having various mole ratios of Mg/Ti obtained by measuring the amount of THF formed during decomposition. The $TiCl_4(THF)_2$ complex was decomposed at 125, 154, and 254 °C as shown in Figure 5a, whereas the $MgCl_2(THF)_2$ complex was decomposed at 86, 156, and 199 °C as shown in Figure 5f. When the Mg/Ti ratio increased, the TPD spectrum of the Mg–Ti

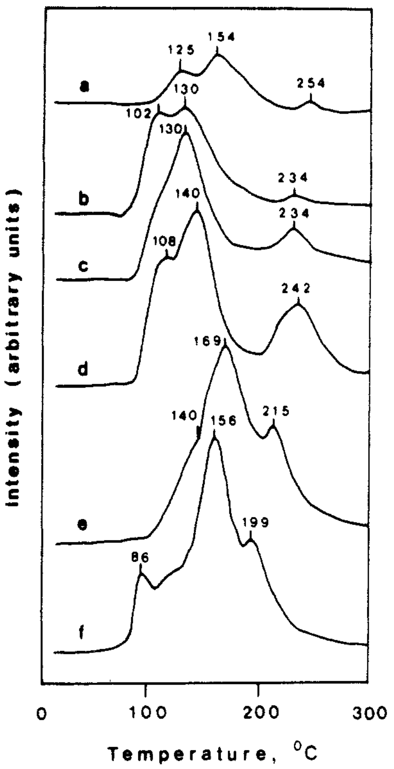


Figure 5. Temperature-programmed decomposition spectra of $MgCl_2/THF/TiCl_4$ bimetallic complex catalysts. Experimental conditions: heating rate = 10 °C/min; N_2 flow rate = 45 cm^3/min; catalyst weight = 0.5 g: (a) Mg/Ti = 0, (b) Mg/Ti = 1.0, (c) Mg/Ti = 2.1, (d) Mg/Ti = 5.2, (e) Mg/Ti = 16.5, (f) Mg/Ti = ∞.

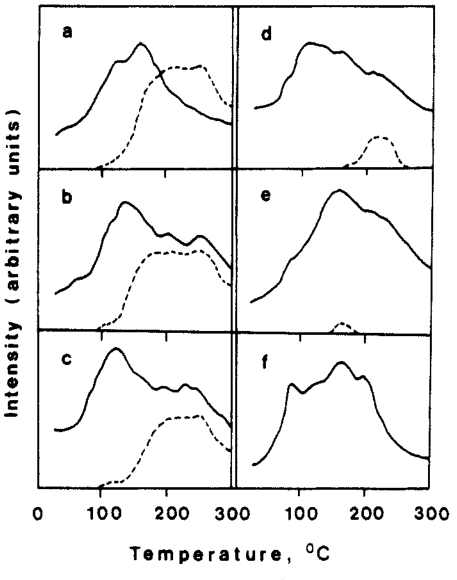


Figure 6. Temperature-programmed mass spectra for THF (—) and 1,4-dichlorobutane (- - -) formed during thermal treatment of $MgCl_2/THF/TiCl_4$ bimetallic complex catalysts: (a) Mg/Ti = 0, (b) Mg/Ti = 1.0, (c) Mg/Ti = 2.1, (d) Mg/Ti = 5.2, (e) Mg/Ti = 16.5, (f) Mg/Ti = ∞.

bimetallic complex became similar to that of the $MgCl_2(THF)_2$ complex. When the Mg/Ti ratio decreased, the TPD spectrum of the bimetallic complex became similar to that of the $TiCl_4(THF)_2$ complex. THF coordinated to $MgCl_2$ and $TiCl_4$ decomposed below 199 and 254 °C, respectively, indicating that THF coordinates to $TiCl_4$ more strongly than to $MgCl_2$.

Temperature-programmed formation spectra of THF and 1,4-dichlorobutane are shown in Figure 6. Mass-to-charge ratios of 42 and 55 are selected to measure the relative amounts of THF and 1,4-dichlorobutane, respectively, based on the highest intensity of mass cracking peaks of THF and 1,4-dichlorobutane as shown in Table I.[8] When the Mg/Ti ratio increased, the amount of 1,4-dichlorobutane formed during thermal decomposition decreased. 1,4-Dichlorobutane was not formed during the thermal decomposition of the $MgCl_2(THF)_2$ complex. These results indicate that some of THF coordinated to Ti is decomposed by thermal treatment and reacted with adjacent Cl to form 1,4-dichlorobutane. THF decomposed above 200 °C is the THF coordinated to Ti because $TiCl_4$ is more Lewis acidic than $MgCl_2$.

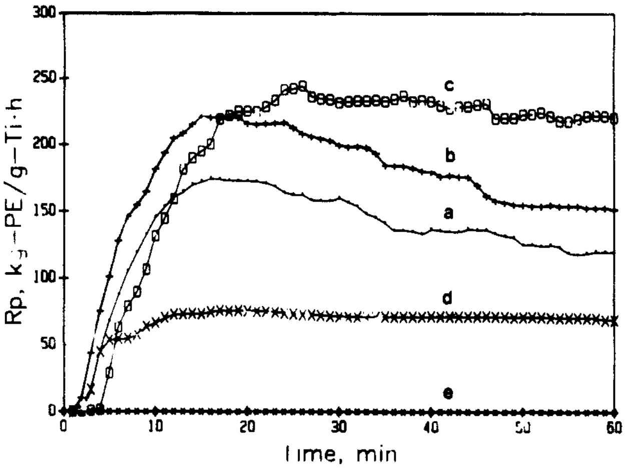


Figure 7. Ethylene polymerization rate profiles after thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2). Thermal treatment conditions: (a) none; (b) 80 °C, 5 min; (c) 108 °C, 5 min; (d) 140 °C, 5 min; (e) 242 °C, 5 min. Polymerization conditions: $P_{C_2H_4}$ = 3 kg$_f$/cm^2; T = 70 °C; $[AlEt_3]/[TiCl_4]$ = 128.

Figure 7 shows ethylene polymerization rate profiles after thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at various temperatures. When the temperature of thermal treatment increased from 80 to 108 °C, the polymerization rate increased. This might be due to the formation of new active site after decoordination of THF which cannot be removed by $AlEt_3$. However, when the temperature of thermal treatment increased above 140 °C, the catalytic activity of polymerization decreased, indicating that titanium active sites started to decompose above 140 °C. When the catalyst was heated at 242 °C, ethylene was not polymerized. A $TiCl_4$-containing precursor having the formula $Mg_3TiCl_{10}(THF)_8$ was prepared and heated in N_2 at 130 °C for 5 h by Karol et al.[14] Productivity decreased to 433 g/(mmol of Ti·h·100 psi C_2H_4) as compared to 2200 g/(mmol of Ti·h·100 psi C_2H_4) for unheated $TiCl_4$-containing precursor. Therefore, our result agrees with Karol's result.

Figure 8 shows ethylene polymerization rate profiles affected by the thermal treatment time of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 80 °C. The treatment times were varied between 5 and 240 min. The thermal treatment at 80 °C for 5 min increased the polymerization rate. The longer thermal treatment (60 and 240 min) slightly decreased the polymerization rate. This indicated that the stability of the active site was hardly affected by the thermal treatment time at 80 °C and that thermal stability was maintained.

Figure 9 shows ethylene polymerization rate profiles after thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 108 °C for 5 min and 1 h, respectively. When the time of thermal treatment increased, the activity of polymerization increased. This fact indicates that more active sites are formed after the

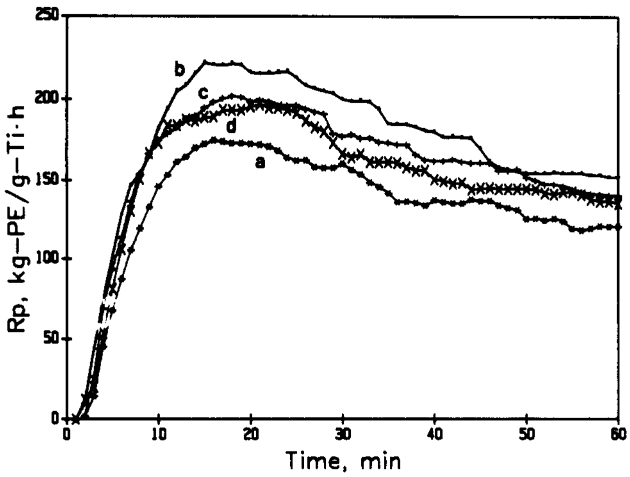


Figure 8. Ethylene polymerization rate profiles after thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 80 °C: (a) 0 min, (b) 5 min, (c) 60 min, (d) 240 min. Polymerization conditions: $P_{C_2H_4} = 3$ kg$_f$/cm^2; $T = 70$ °C; $[AlEt_3]/[TiCl_4] = 128$.

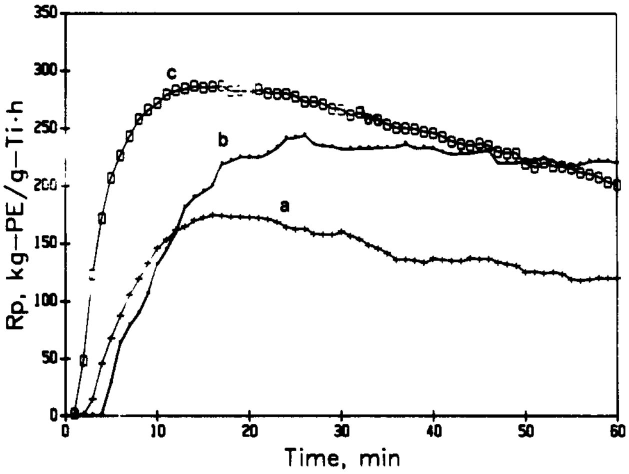


Figure 9. Ethylene polymerization rate profiles after thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) at 108 °C: (a) 0 min, (b) 5 min, (c) 60 min. Polymerization conditions: $P_{C_2H_4} = 3$ kg$_f$/cm^2; $T = 70$ °C; $[AlEt_3]/[TiCl_4] = 128$.

Table II
Infrared Bands of $MgCl_2/THF/TiCl_4$ Bimetallic Complex Catalysts after Thermal Treatments

Mg/Ti (obsd)	treatment temp (°C)	treatment time (min)	diagnostic IR bands (cm^{-1})
5.2			1034, 964, 921, 885
5.2	80	5	1034, 964, 920, 885
5.2	108	5	1033, 962, 919, 884
5.2	140	5	1024, 960, 920, 879
5.2	242	5	1022
5.2	80	60	1033, 961, 919, 884
5.2	108	60	1031, 963, 919, 884
5.2	140	30	1023, 959, 920, 878
5.2	140	60	1022, 958, 919, 878
16.5			1036, 957, 919, 885
16.5	80	5	1035, 963, 921, 885
16.5	140	5	1034, 958, 921, 884

more strongly coordinated THF which can be detached at 108 °C is separated. The thermal stability of the catalyst was maintained at 108 °C.

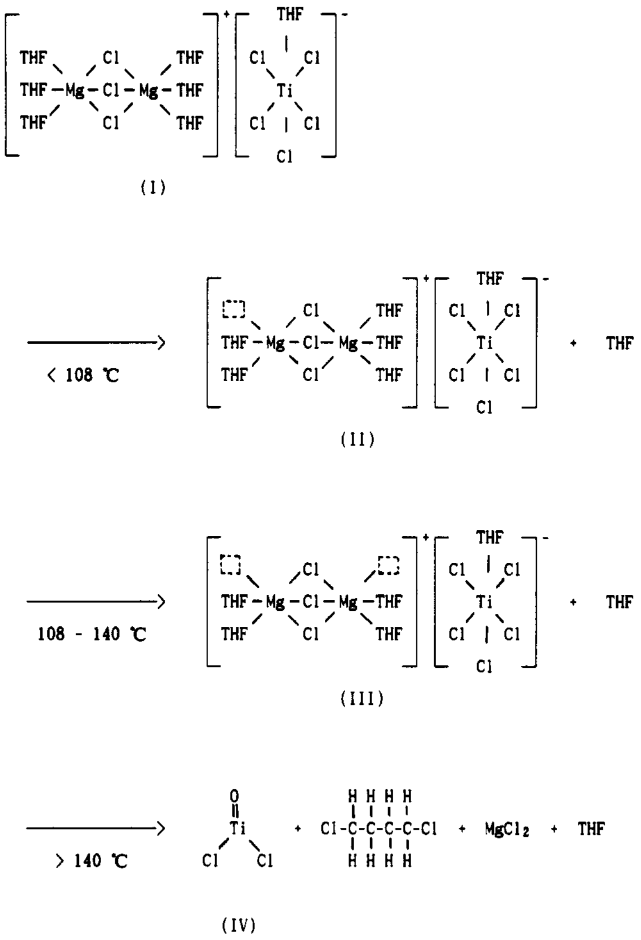


Figure 10. Plausible change in the structure of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) during thermal treatment.

Table II shows the diagnostic infrared bands of $MgCl_2/THF/TiCl_4$ bimetallic complex catalysts after various thermal treatments. The infrared spectrum of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) has an asymmetrical C–O–C stretching band at 1034 cm^{-1} and a symmetrical C–O–C stretching band of THF at 885 cm^{-1}.[2,9] These asymmetrical and symmetrical C–O–C stretching bands of THF were not shifted after thermal treatment at 80 °C for 5 min. When the thermal treatment temperature of the catalyst increased above 140 °C, these bonds were shifted to lower frequencies. This red-shift might be due to the decoordination of THF weakly coordinated to $MgCl_2$ or $TiCl_4$. After thermal treatment at 140 °C, the remaining THF is strongly coordinated to $TiCl_4$, resulting in lower C–O–C stretching bands because more electrons are transferred from the oxygen atom of THF to Lewis acidic $TiCl_4$. The catalytic activity of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) after thermal treatment at 140 °C decreased significantly as shown in Figure 7. There are two plausible explanations for this fact. The $MgCl_2/THF/TiCl_4$ bimetallic complex containing strongly coordinated THF either is less active or cannot be activated by $AlEt_3$. Furthermore, the formation of 1,4-dichlorobutane above 140 °C indicates that the catalytic $TiCl_4$ species start to decompose.

In Figure 10 is suggested the plausible change in the structure of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) during thermal treatment. When the Mg/Ti ratio of this catalyst is 5.2, this catalyst is a mixture of the ionic salt $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+[TiCl_5(THF)]^-$ and $MgCl_2(THF)_2$, which was elucidated by Sobota et al.[5] Therefore, structure I is only used in this model because $MgCl_2$ is not an active site. When this complex is heated below 108 °C, THF is the only product as shown in Figure 6 and the activity of polymerization increases as shown in Figure 7. Therefore, structure II is suggested. In this case it is supposed that some preliminary active sites are activated because THF coordinated to the catalytic active site is separated during thermal treatment.

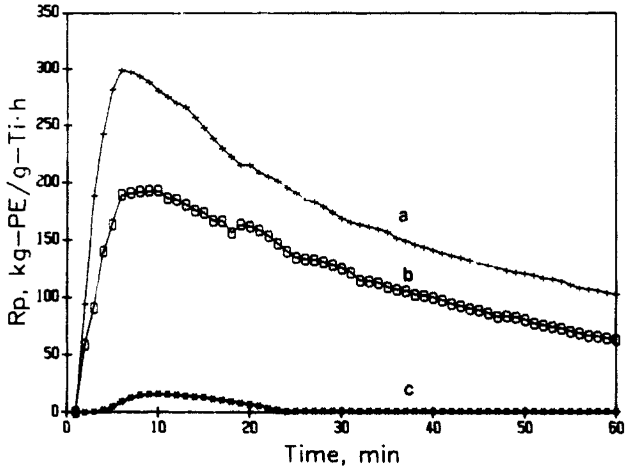


Figure 11. Ethylene polymerization rate profiles after thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 16.5). Thermal treatment conditions: (a) none; (b) 80 °C, 5 min; (c) 140 °C, 5 min. Polymerization conditions: $P_{C_2H_4} = 3\ kg_f/cm^2$; $T = 70$ °C; $[AlEt_3]/[TiCl_4] = 128$.

After thermal treatment at 140 °C, THF is decoordinated but the activity of polymerization decreases because the thermal stability of the catalytic active site is not maintained. Therefore, structure III which has double vacancy is suggested. It is supposed that when the catalyst is heated above 140 °C, the ionic salt of structure III starts to decompose, resulting in the formation of 1,4-dichlorobutane and inactive species IV.

Figure 11 shows ethylene polymerization rate profiles after thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 16.5) at various temperatures for 5 min. The activity of this catalyst decreases even after heating at 80 °C for 5 min. It is supposed that the thermal stability of the catalytic active site is not maintained after thermal treatment because of destruction of the catalyst structure. The infrared spectrum of the catalyst is characterized by the asymmetrical C–O–C stretching band at 1036 cm^{-1} and the symmetrical C–O–C stretching band of THF at 885 cm^{-1} as shown in Table II.[2,9] The asymmetrical and symmetrical C–O–C stretching bands of THF are hardly shifted after thermal treatment. As shown in Figure 6e, most of THF is coordinated to $MgCl_2$ and 1,4-dichlorobutane is formed at a small amount, indicating that amount of THF remaining after thermal treatment coordinated to $TiCl_4$ is small. Hence, the C–O–C stretching band was not changed very much after thermal treatment.

Conclusions

THF and 1,4-dichlorobutane were produced during the thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst. THF coordinated to the different sites of this catalyst was decomposed at different temperatures depending on the Mg/Ti ratios. The amount of 1,4-dichlorobutane formed during thermal treatment decreased with an increase in the Mg/Ti ratio. 1,4-Dichlorobutane was not observed during the thermal treatment of the $MgCl_2(THF)_2$ complex, indicating that THF coordinated to Mg was simply decoordinated during thermal treatment. THF coordinated to $TiCl_4$ was decoordinated at temperatures higher than THF coordinated to $MgCl_2$ because of the Lewis acidity of $TiCl_4$ being stronger than that of $MgCl_2$. Some of THF coordinated to Ti was decomposed by thermal treatment and reacted with adjacent Cl from $TiCl_4$, resulting in the formation of 1,4-dichlorobutane. When the temperature of thermal treatment of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 5.2) was below 108 °C, the catalytic activity of polymerization increased, while it decreased above 140 °C. However, the catalytic activity of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst (Mg/Ti = 16.5) decreased after thermal treatment at 80 °C, indicating that the thermal stability of the $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst at the higher ratio of Mg/Ti decreased.

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