

TEMPERATURE PROGRAMMED DECOMPOSITION OF SILICA-SUPPORTED $MgCl_2/THF/TiCl_4$ CATALYST AND EFFECT OF THERMAL TREATMENT ON ETHYLENE POLYMERIZATION RATE

Young Soo Ko, Taek Kyu Han and Seong Ihl Woo[†]

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
373-1 Kusong-dong, Yusong-gu, Taejeon 305-701, Korea
(Received 10 February 1997 • accepted 14 August 1997)

Abstract – Silica supported $MgCl_2/THF/TiCl_4$ catalyst ($SiO_2/MgCl_2/THF/TiCl_4$) was prepared, and then decomposed thermally. The amount of produced gas [tetrahydrofuran (THF) and 1,4-dichlorobutane (DCB)] was measured with gas chromatography (GC) and mass spectrometer. $SiO_2/MgCl_2/THF/TiCl_4$ catalyst started to decompose around 85 °C, and further decomposed at 113, 150 and 213 °C. THF was mainly produced, but very small amount of DCB evolved during temperature programmed decomposition (TPD), while unsupported $MgCl_2/THF/TiCl_4$ produced DCB significantly. Polymerization rate of ethylene with $SiO_2/MgCl_2/THF/TiCl_4$ decreased when it was preheated at 85 and 110 °C for 5 and 60 min, respectively, while that of unsupported $MgCl_2/THF/TiCl_4$ increased after same pretreatment condition. It can be suggested that Mg/Ti bimetallic complex anchored on the surface of silica through OH group of it has weak interaction between Mg and Ti species.

Key words: Olefin Polymerization, Ziegler-Natta Catalyst, Silica, Thermal Treatment

INTRODUCTION

A $MgCl_2/THF/TiCl_4$ bimetallic complex catalyst showed very high activity in ethylene homopolymerization [Han et al., 1989; Kim and Woo, 1989]. This catalyst also showed that the activity of ethylene polymerization increased as the Mg/Ti atomic ratio in catalyst increased in the range of 0.4 and 16.5. This has been explained as follows; at higher Mg/Ti atomic ratio, the cationic Mg complex interacts with anionic Ti complex to form cluster bound weakly each other because Ti complex are diluted by $MgCl_2 \cdot THF$ complex. This can increase in active sites due to ease fragmentation of catalysts during the polymerization [Kim et al., 1990].

In the case of the Mg/Ti atomic ratio of 5.2 in bimetallic complex, polymerization rate of ethylene increased when it was thermally treated below 108 °C [Choi et al., 1993]. 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 [Choi et al., 1993]. This indicates that the thermal stability of $MgCl_2/THF/TiCl_4$ catalyst (Mg/Ti=16.5) is worse than that of the Mg/Ti atomic ratio of 5.2. It was elucidated from Temperature Programmed Decomposition (TPD) experiments that tetrahydrofuran (THF) was decomplexed from the bimetallic complex during heating, and that thermal treatment of bimetallic catalyst can influence on the kinetics of polymerization [Choi et al., 1993] and copolymerization [Ko et al., 1994, 1997], and on comonomer distribution significantly [Ko et al., 1997].

$SiO_2/MgCl_2/THF/TiCl_4$ was developed to establish excellent morphology control of polymer particle in the fluidized bed reactor [Wagner et al., 1981]. We reported the characteristics of $SiO_2/MgCl_2/THF/TiCl_4$ catalyst in the ethylene polymerization [Kim et al., 1990; Kim and Woo, 1990], and ethylene-1-butene copolymerization [Kim et al., 1994].

In this study, TPD study of $SiO_2/MgCl_2/THF/TiCl_4$ was performed to examine the effect of immobilization of $MgCl_2/THF/TiCl_4$ on the surface of silica. The effect of thermal treatment of $SiO_2/MgCl_2/THF/TiCl_4$ catalyst on the ethylene polymerization rate was also investigated.

EXPERIMENTAL

The polymerization grades of ethylene (Daelim Ltd., Korea) and nitrogen of extra pure grade were further purified with the columns of Fisher RIDOX and molecular sieve 5A/13X. Silica gel (Davison 952) was dehydrated at 500 °C for 12 hrs in a nitrogen condition. *n*-Hexane (Duksan Ltd., Korea) of extra pure grade was further purified by reflux over sodium metal in a nitrogen atmosphere. The analytic grade of tetrahydrofuran (J. T. Baker Chemical Co., Phillipsburg, NJ) was purified by distillation under reflux with $LiAlH_4$ for several hours. Anhydrous magnesium chloride (Aldrich), aluminium triethyl (Aldrich), and $TiCl_4$ (Aldrich) were used without further purification. The $SiO_2/MgCl_2/THF/TiCl_4$ catalyst (Mg/Ti atomic ratio=5.2) was prepared by reaction between $MgCl_2(THF)_2$ and $TiCl_4(THF)_2$, and then yellow precursor solution was impregnated to dehydrated silica gel. Ti content in the prepared catalyst was 0.54 mmol-Ti/g-catalyst. Slurry poly-

[†]To whom all correspondence should be addressed.

merization was carried out in a 1-L autoclave under a constant pressure of ethylene at 70 °C. The detailed procedures for catalyst synthesis [Kim et al., 1990] and polymerization [Kim et al., 1990] were described elsewhere. The TPD experiment was conducted under a helium 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. Mass spectra were obtained with a VG SX300 quadrupole spectrometer during TPD of the catalysts.

RESULTS AND DISCUSSION

In Fig. 1(a) is shown the TPD spectrum of the $\text{SiO}_2/\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ catalyst. TPD spectrum of silica supported bimetallic catalyst was different from that of $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ catalyst. The $\text{SiO}_2/\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ catalyst was decomposed at 113, 150 and 213 °C, while $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ ($\text{Mg}/\text{Ti}=5.2$) was decomposed at 108, 140 and 242 °C [Choi et al., 1993]. The gaseous products were identified as THF and DCB by MS, FT-IR and ^{13}C -NMR experiments. THF coordinated to MgCl_2 decomposed at 86, 156 and 199. THF coordinated to TiCl_4 decomposed at 125, 154 and 254 °C. This result indicates that THF coordinates to TiCl_4 more strongly than to MgCl_2 [Choi et al., 1993]. To confirm the relative amount of THF and DCB the gaseous products during the TPD of silica supported bimetallic catalyst, the experiments of temperature programmed formation spectra of THF and DCB were performed and its results are shown in Fig. 2. Mass to charge ratios of 42 and 55 are selected to measure the relative amounts of THF and DCB, respectively, based on the highest intensity of mass cracking peaks of THF and DCB. As shown in Fig. 2, very small amount of DCB was formed during TPD and THF was a main gaseous product.

In the case of $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ bimetallic complex catalyst, DCB was generated at 242 °C, resulting from the reaction of THF and Cl coordinated to Ti species. From TPD result described above, bimetallic catalyst supported on the surface of silica produced very little amount of DCB. From this

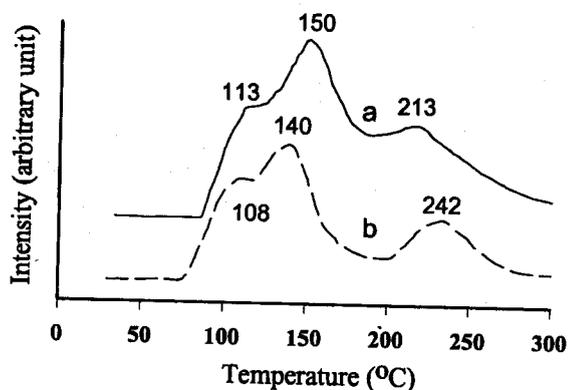


Fig. 1. Temperature programmed decomposition spectrum of the $\text{SiO}_2/\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ (a) and $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ (b). Heating rate=10 °C/min; He flow rate=50 cm^3/min ; catalyst weight=0.5 g.

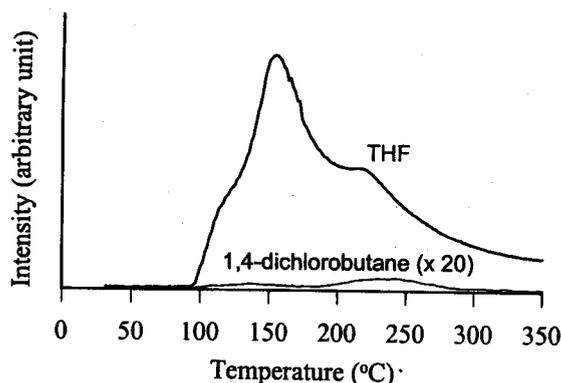


Fig. 2. Temperature programmed formation mass spectra of THF and 1,4-dichlorobutane for $\text{SiO}_2/\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ bimetallic complex catalyst.

result, it would be suggested that there was little THF coordinated to TiCl_4 to form DCB from the reaction with Cl of TiCl_4 because THF exists hardly at Ti active species during the preparation of silica supported bimetallic complex catalyst.

Choi et al. suggested the plausible change in the structure of the $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ bimetallic complex as shown in Fig. 3(a) [Choi et al., 1993]. When Mg/Ti atomic ratio of this complex is higher than 2, this complex is a mixture of the ionic salt $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+[\text{TiCl}_3(\text{THF})]^-$ and $\text{MgCl}_2(\text{THF})_2$, which is elucidated by Sobota and Utko [Sobota and Utko, 1988]. This structure can be suggested when it is presented in the form of single crystal or solid powder. A $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ catalyst was prepared by precipitation of solution of $\text{MgCl}_2(\text{THF})_2$ and $\text{TiCl}_4(\text{THF})_2$ with 1-hexane. Therefore, the structure of $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ catalyst can be speculated as that reported by Sobota et al. From this structure, it can be explained that DCB can be generated due to the presence of THF adjacent to Ti in this ionic salt at higher temperature.

In the case of $\text{SiO}_2/\text{MgCl}_2/\text{THF}/\text{TiCl}_4$, the plausible mechanism of the reaction of SiO_2 with TiCl_4 was proposed by several authors [Soga et al., 1983; Chien and Hsieh, 1976; Munoz-Escalona et al., 1984]. In the present study, active precursor solution prepared from the dissolving MgCl_2 and TiCl_4 in THF reacted with hydroxyl groups of the silica without the precipitation process and its plausible structure is shown in Fig. 3(b) [Kim et al., 1990]. Species (E), which is prepared at higher Mg/Ti atomic ratio, has four bridged and two terminal chlorine atom, and can react with one hydroxyl group due to the less reactivity of bridged chlorine. As shown in Fig. 3(b), there is no THF adjacent to the Ti atom, resulting in the smaller generation of DCB during thermal treatment of $\text{SiO}_2/\text{MgCl}_2/\text{THF}/\text{TiCl}_4$.

Fig. 4 shows the ethylene polymerization rate profiles after thermal treatment of the silica supported bimetallic catalyst at 85 °C and 110 °C for 5 and 60 min. When the temperature of thermal treatment was raised, the polymerization rate decreased. It can be suggested that the thermal stability of the catalytic active site on the surface of silica is not maintained after thermal treatment. However, unsupported $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ bimetallic complex catalyst showed thermal stability at 80 and 108 °C [Choi et al., 1993]. When unsupported

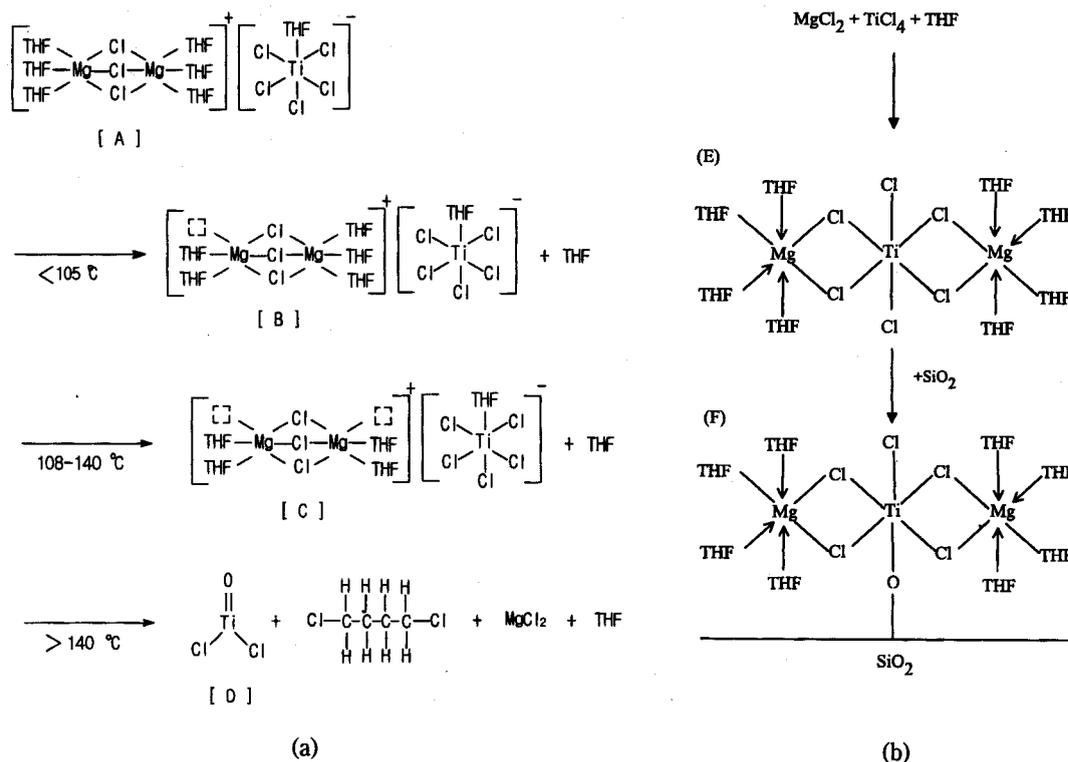


Fig. 3. Plausible change of structure of $MgCl_2/THF/TiCl_4$ during heating (a) and plausible structure of Mg/Ti bimetallic complexes attached to the surface of silica (b).

ed $MgCl_2/THF/TiCl_4$ bimetallic catalyst was treated thermally at $80^\circ C$ and $108^\circ C$, polymerization rate of ethylene was increased. Choi et al. have elucidated that the enhancement of polymerization rate after thermal treatment below $108^\circ C$ might be due to the formation of new active site after decoordination of THF, and that the polymerization rates of ethylene decreased as thermal treatment temperature increased to $140^\circ C$, resulting from decomposition of catalytically active $TiCl_3(THF)$ at higher temperature [Choi et al., 1993]. Fig. 4 also shows that ethylene polymerization rate profiles were affected by the thermal treatment time of the $SiO_2/MgCl_2/THF/TiCl_4$ bimetallic complex catalyst at 85 and $110^\circ C$. The longer thermal treatment (60 min) slightly decreased the polymerization rate. This indicated that the stability of the active site was not affected by the thermal treatment time, but by the thermal treatment temperature. These different behavior of polymerization rate after thermal treatment between $MgCl_2/THF/TiCl_4$ and $SiO_2/MgCl_2/THF/TiCl_4$ catalyst would come from the bonding and interaction between OH of silica gel and Mg/Ti bimetallic complex as shown in Fig. 3(b). Murata et al. have reported that SiO_2 is not an inert support but a reactive support which affects active species to change chemical properties from the results of XPS study and investigation of k_p value for silica supported Mg-Ti catalyst [Murata et al., 1990]. The binding energy of Ti_{2p} for supported catalyst was increased about 0.3 eV in comparison with that of Mg-Ti catalyst, indicating that the electron density of Ti of supported catalyst decreased. Soga et al. also claimed from the experiments of washing of catalyst that $MgCl_2$ forms a weak complex with Ti species on the surface of silica and it can

be removed easily by washing with THF [Soga et al., 1983]. From these results described above, it could be suggested that thermal treatment would decompose readily the Mg/Ti bimetallic complex anchored on the surface of silica because of weak interaction between Mg and Ti, resulting in decoordination of Mg species from Ti species. This, therefore, ma-

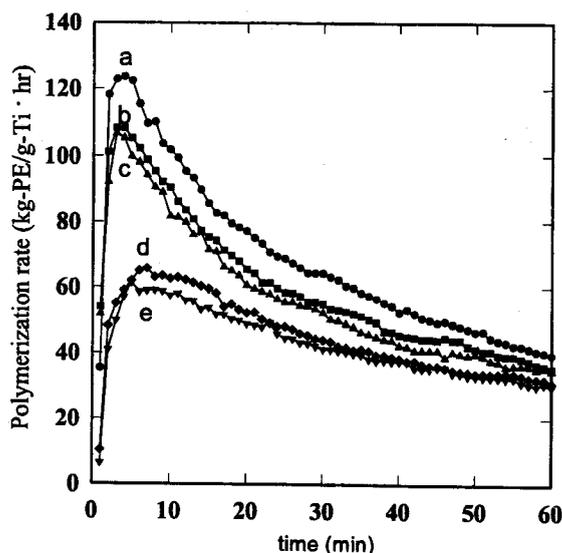


Fig. 4. Ethylene polymerization rate profiles after thermal treatment of the $SiO_2/MgCl_2/THF/TiCl_4$ catalyst. Thermal treatment conditions; (a) none; (b) $85^\circ C$, 5 min; (c) $85^\circ C$, 60 min; (d) $110^\circ C$, 5 min; (e) $110^\circ C$, 60 min (Polymerization condition: $P_r=3$ atm; $T=70^\circ C$, $[Al]/[Ti]=128$).

kes the Mg/Ti atomic ratio lower than that of not thermally pretreated one. It was known that when the Mg/Ti atomic ratio in the complex decreased, the catalytic activity decreased due to the lower catalytic activity of Mg/Ti bimetallic complex itself.

In conclusion, $\text{SiO}_2/\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ was decomposed at 85, 113, 150 and 213 °C and main gaseous product was THF during decomposition. Polymerization rates decreased as preheating temperature increased, indicating that Mg species should be detached from Ti species due to the weak interaction between them.

ACKNOWLEDGMENT

This research was funded by the National Project granted from the Ministry of Science and Technology (Grant N04900).

REFERENCES

- Chien, J. C. W. and Hsieh, J. T. T., "Supported Catalysts for Stereospecific Polymerization of Propylene", *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 1915 (1976).
- Choi, H. K., Chung, D. W., Han, T. K. and Woo, S. I., "Temperature-Programmed Decomposition of a $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ Bimetallic Complex Catalyst and Its Effect on Ethylene Polymerization Rate", *Macromolecules*, **26**, 452 (1993).
- Han, J. D., Kim, I. and Woo, S. I., "Kinetics of Ethylene Polymerization by Coprecipitated $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ Catalyst", *Polymer (Korea)*, **13**, 147 (1989).
- Kim, I. and Woo, S. I., "Homo- and Co-polymerization of Ethylene with Highly Active Ti/Mg Bimetallic Complexes, Effect of Crystallization Conditions on Structure and Productivity", *Polym. Bull.*, **22**, 239 (1989).
- Kim, I., Chung, M. C., Choi, H. K., Kim, J. H. and Woo, S. I., "Homo- and Co-polymerization of Ethylene with the Highly Active $\text{TiCl}_4/\text{THF}/\text{MgCl}_2$ Catalyst", *Catalytic Olefin Polymerization*, Kodansha Ltd., Tokyo, 323 (1990).
- Kim, I., Kim, J. H. and Woo, S. I., "Kinetic Study of Ethylene Polymerization by Highly Active Silica Supported $\text{TiCl}_4/\text{MgCl}_2$ Catalyst", *J. Appl. Polym. Sci.*, **39**, 837 (1990).
- Kim, I. and Woo, S. I., "Kinetic Study for the Decay Rate of Ethylene Polymerization Catalyzed over Silica Supported $\text{TiCl}_4/\text{MgCl}_2$ Catalysts", *KJChE*, **7**, 95 (1990).
- Kim, J. H., Jeong, Y. T. and Woo, S. I., "Copolymerization of Ethylene and 1-Butene with Highly Active $\text{TiCl}_4/\text{THF}/\text{MgCl}_2$, $\text{TiCl}_4/\text{THF}/\text{MgCl}_2/\text{SiO}_2$, and $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ Catalysts", *J. Polym. Sci. Part A: Polym. Chem.*, **32**, 2979 (1994).
- Ko, Y. S., Han, T. K. and Woo, S. I., "Temperature Programmed Decomposition of $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ Bimetallic Complex Catalyst and its Effect on the Homo- and Copolymerization of Ethylene", *Catalyst Design for Tailor-Made Polyolefins*, Kodansha Ltd., Tokyo, 163 (1994).
- Ko, Y. S., Han, T. K., Park, J. W. and Woo, S. I., "Copolymerization of Ethylene and 1-Hexene with Thermally Pretreated $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ Bimetallic Catalyst", *J. of Polym. Sci. Part A. Polym. Chem.*, in press (1997).
- Ko, Y. S., Han, T. K., Park, J. W., Sadatoshi, H. and Woo, S. I., "Analysis of Microstructure of Ethylene-1-Hexene Copolymer Prepared over Thermally Pretreated $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ Bimetallic Catalyst", *J. of Polym. Sci. Part A. Polym. Chem.*, in revision (1997).
- Munoz-Escalona, A., Hernandez, J. G. and Gallardo, J. A., "Catalytic Activity and Control of the Nascent Morphology of Polyethylenes Obtained with First and Second Generation of Ziegler-Natta Catalysts", *J. Appl. Polym. Sci.*, **29**, 1187 (1984).
- Murata, M., Nakano, A., Furuhashi, H. and Imai, M., "Development of SiO_2 -Supported Type Catalyst for Propylene Polymerization", *Catalytic Olefin Polymerization*, Kodansha Ltd., Tokyo, 165 (1990).
- Sobota, P. and Utko, J., " MgCl_2 -factor Controlling the Reaction Mechanism of Olefin Polymerization", *Polym. Commun.*, **29**, 144 (1988).
- Soga, K., Ohnishi, R. and Doi, Y., "Copolymerization of Ethylene with Propylene over SiO_2 -Supported $\text{MgCl}_2/\text{TiCl}_4$ Catalyst", *Polym. Bull.*, **9**, 299 (1983).
- Wagner, B. E., Goeke, G. L., Karol, F. J. and Goerge, K. F., "Continuous Production of Ethylene (Co)polymers by Contacting Monomer with Catalyst Containing Reaction Product of Magnesium Cpd. with Electron Donor", *Eur. Pat. Appl.* 0,055,605 (1981).