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Copolymerization of Ethylene with Propylene over SiO_2-Supported $MgCl_2/TiCl_4$ Catalyst

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Summary

The SiO_2-supported $TiCl_4$ catalyst was prepared by allowing SiO_2 to react with $TiCl_4$ in n-heptane. Then $MgCl_2$ was supported onto this catalyst by treating a mixture of this catalyst and $MgCl_2 \cdot (THF)_2$ with $AlEt_2Cl$ in n-heptane. The SiO_2-supported $MgCl_2/TiCl_4$ catalyst thus prepared showed a very high activity for the copolymerization of ethylene and propylene and gave a moderately random copolymer. A plausible model for the active species was proposed from the analytical results of the catalytic system.

Introduction

A large number of patents and publications claim the synthesis of random and block copolymers from ethylene and propylene (BOOR 1979). The copolymer composition strongly depends on the catalytic systems. Soluble catalysts such as $VOCl_3$ and VCl_4 combined with $Al(C_2H_5)_2Cl$ give a random or moderately alternating copolymer. On the other hand, heterogeneous catalysts which seem to contain multiple active species usually give block copolymers.

We have recently found that Ti(III) species are active both for ethylene and propylene polymerization, while the Ti(II) species are active only for ethylene polymerization (SOGA et al. 1981). Therefore, random copolymer will be produced even by using the heterogeneous catalysts composed of titanium, if it is possible to prevent the Ti(III) species from over-reduction. On the basis of this assumption, we have obtained a considerably random copolymer from the copolymerization of ethylene and propylene over the SiO_2-supported $MgCl_2/TiCl_3$ catalyst combined with $Al(C_2H_5)_3$ (SOGA et al. 1982). It is known that the $\geqslant$Si-O-Ti(III)Cl_2 species formed from the reaction between the surface hydroxyl groups of SiO_2 and $TiCl_4$ in n-heptane followed by reduction with aluminum alkyls are extremely stable even in the presence of $Al(C_2H_5)_3$. Therefore, this SiO_2-supported $TiCl_4$ catalyst seems to be excellent for the random copolymerization. On the other hand, we have already reported that the activity for propylene polymerization drastically increases by coexisting of only a small amount of $MgCl_2$ in the catalytic systems of $MgCl_2/TiCl_3/SiO_2$ combined with $Al(C_2H_5)_3$ (SOGA et al. 1981). It is still unknown, however, whether such a marked improvement on the activity is also caused by the addition of $MgCl_2$ to the $\geqslant Si\text{-}O\text{-}TiCl_2$ species.

In the present study, the copolymerization of ethylene with propylene was carried out by using the SiO_2-supported $TiCl_4$ catalyst combined with $Al(C_2H_5)_3$, and the activating effect of $MgCl_2$ was also examined.

Experimental

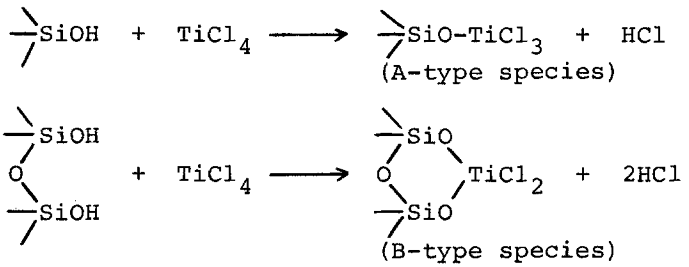
Materials Research grade ethylene, propylene and n-heptane (from Takachiho Chemical Co.) were purified according to the same procedures reported earlier (SOGA et al. 1980). SiO_2 (from Fuji Davison Co., 300 m^2/g) was evacuated at 300 °C for 4 h immediately before use. Nitrogen of ultra high purity (from Nihon Sanso Co., 99.9989 %) was purified by passing through the molecular sieve 3A column cooled at -196 °C. The other chemicals (research grade) were commercially obtained and used without further purification.

Preparation of the SiO_2-supported $TiCl_4$ catalyst To a 200 ml glass reactor equipped with a magnetic stirrer were added 90 ml of n-heptane, 10 g of SiO_2 and 40 ml of $TiCl_4$ under nitrogen. The mixtures were kept standing with vigorous stirring for 6 h at 98.4 °C. To the reactor containing the precipitates was added 40 ml of n-heptane, and the mixtures were again kept standing with vigorous stirring for 6 h at room temperature to remove the unreacted $TiCl_4$. Then, the precipitates were separated by filtration under nitrogen atmosphere, adequately washed with n-heptane and evacuated at room temperature for 6 h, at 90 °C for 6 h and then at 300 °C for 4 h.

Copolymerization and analytical procedures The copolymerization of ethylene and propylene was usually carried out in a conventional gas circulation system with the same procedures reported earlier (SOGA et al. 1982). The copolymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The precipitate was dried i. vac. at room temperature overnight. The amounts of titanium and magnesium included in the catalyst were determined by atomic absorption spectrophotometry (Shimadzu AA-6105). The ESR spectrum was taken in a pyrex glass tube of 3 mm diameter at room temperature on a JEOL JES-PX-IX ESR spectrometer with $100 \cdot 10^3$ cycles per s field modulation. 1,1-Diphenyl-2-picryl-hydrazyl (DPPH) and Mn(II) doped on MgO were used to determine the concentration of Ti(III) and the g-value, respectively. The composition of the copolymer was determined by ^{13}C NMR spectrum measured at 120 °C using a JEOL JUM PS-100 spectrometer equipped with the PFT-100 Fourier transform system operating at 25.14 MHz. The solution was made up in trichlorobenzene to 15 w/v%. The chemical sift was represented in ppm downfield from internal tetramethylsilane (TMS). The molecular weight distribution of the copolymer was measured at 150 °C by GPC (Shodex LC HT-3) using o-dichlorobenzene as solvent.

Results and Discussion

The reaction of SiO_2 with $TiCl_4$ was previously found to proceed according to the following equations (SOGA et al. 1980).



The HCl evolved is easily adsorbed on the surface of SiO_2, so it seems very difficult to determine quantitatively the amount of HCl evolved. Therefore, the fractions of A-type (f_A)- and B-type (f_B)- species were conventionally determined from the reaction of $Zn(C_2H_5)_2$ with the surface hydroxyl groups of SiO_2 (f_A = 66 %, f_B = 34 %). The amount of titanium contained in the present catalyst was confirmed to be 0.51 matom Ti/g-cat. The mixture of the catalyst (Cat-I) and $Al(C_2H_5)_2Cl$ (0.50 mol/l) was kept standing at room temperature for 20 h. The color of the catalyst changed from white to yellowish brown by this treatment. The ESR spectrum of the mixture taken at -196 °C displayed a broad signal with the g-value of approximately 1.95 attributable to Ti(III). The time dependence of the formation of Ti(III) followed by ESR showed that the fraction of Ti(III) increased rapidly and reached a constant value near to the fraction of A-type species (66 %). These results strongly indicate that only the A-type species can be reduced by $Al(C_2H_5)_2Cl$ as suggested by CHIEN et al. (1976), and that the over-reduction of the Ti(III) species hardly takes place under the copolymerization conditions.

Then a small amount of $MgCl_2$ was supported on Cat-I according to the following procedures: The complex of $MgCl_2 \cdot (THF)_2$ was prepared by dissolving $MgCl_2$ in THF followed by evacuation at room temperature for 5 h. To 40 ml of n-heptane containing 1.0 g of Cat-I and 20 mmol of $AlEt_2Cl$ was added the measured amount of $MgCl_2 \cdot (THF)_2$ under nitrogen. The mixtures were kept standing with vigorous stirring for 20 h at room temperature. The precipitates were separated by filtration, washed with plenty of n-heptane and dried i. vac. at room temperature.

The precipitates showed green color, which implies the formation of a complex between $MgCl_2$ and the titanium species. This catalyst (Cat-II) combined with $AlEt_3$ or $AlEt_2Cl$ also showed a broad signal with the g-value of approximately 1,95 attributable to Ti(III). Polymerization of propylene was conducted at 65 °C for 15 min in a stainless steel reactor by using both Cat-I and Cat-II. The results obtained are shown in Tab. 1 together with some analytical data of the catalysts. It should be noted that the catalytic activity markedly increased by coexisting only a small quantity of $MgCl_2$.

Table 1. Results of Propylene Polymerization[a)]

Run No.	Catalyst	Ti Supported (matom/g-cat.)	Mg Supported (matom/g-cat.)	Mg/Ti	Activity (kg-pp/g-Ti•h)
1	$TiCl_4/SiO_2$ (Cat-I)	0.51	0	0	0.73
2	$TiCl_4/MgCl_2/SiO_2$ (Cat-II)	"	0.59	1.2	4.09
3	"	"	0.90	1.8	14.8
4	"	"	1.11	2.2	11.9
5	"	"	1.57	3.1	12.5
6	"	"	2.12	4.2	13.9
7	"	"	2.37	4.6	10.6

a) Polymerization was conducted in a stainless steel reactor at 65 °C for 15 min by using 0.1 mmol of $AlEt_3$, 10 ml of n-heptane and 11 g of propylene.

To obtain a better insight into the active species of Cat-II, the following experiments were carried out: To 40 ml of THF was added 1.0 g of Cat-II and the mixture was kept standing with vigorous stirring at room temperatrue for 20 h. The precipitates were separated by filtration under nitrogen, followed by washing with plenty of THF to obtain Cat-II'.

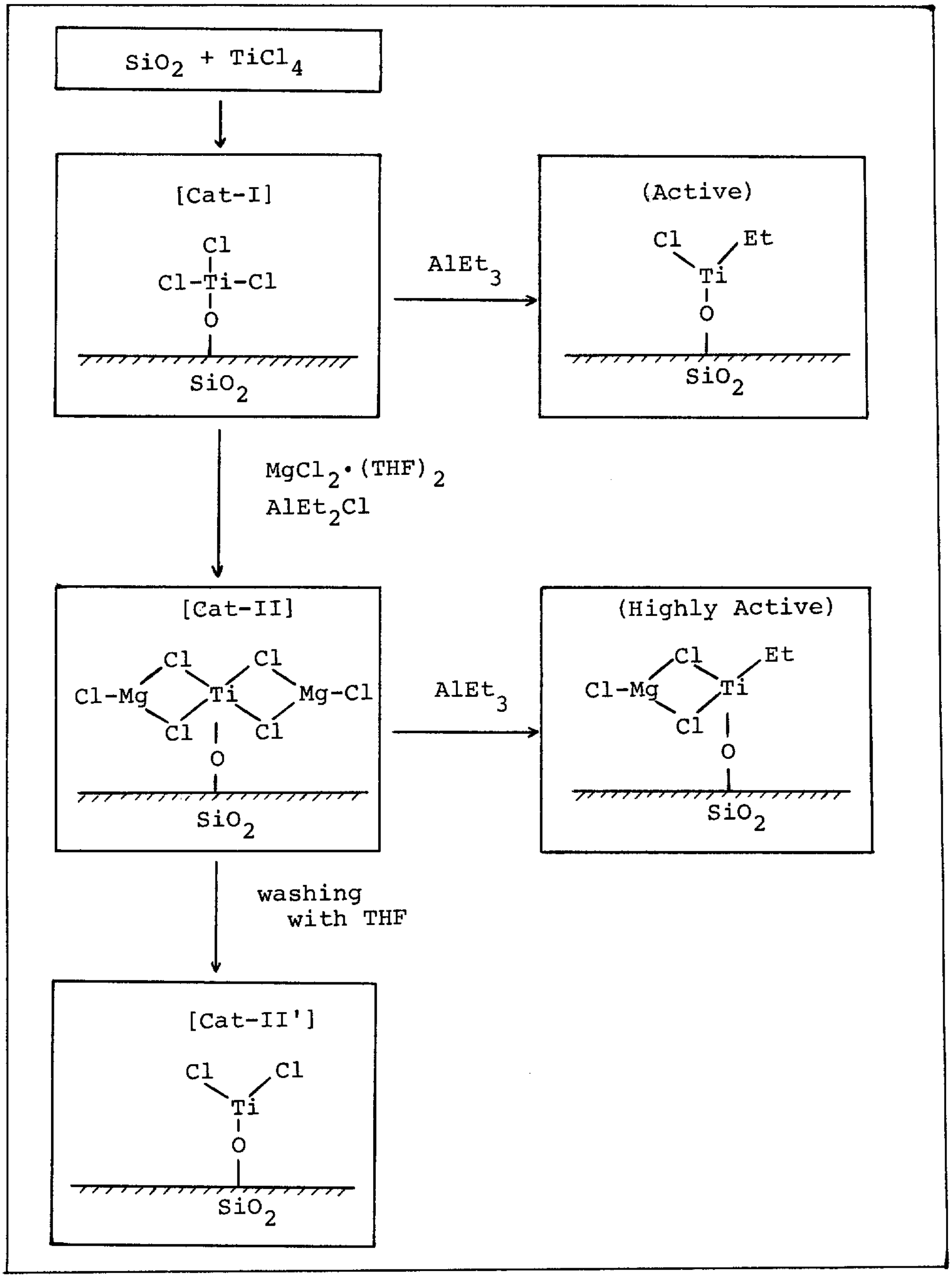
Then both Cat-II and Cat-II' were analyzed by atomic absorption spectrophotometry and elemental analysis. The results (Tab. 2) clearly indicate that the $MgCl_2$ supported on Cat-II is removed almost completely by washing with THF. Therefore it may be said that $MgCl_2$ forms a weak complex with the titanium species. On the other hand, the observed atomic ratio of Cl/Ti (ca. 2) supports the inference previously mentioned that only A-type species are reduced by $AlEt_2Cl$.

Table 2. Analytical Results of Cat-II[a)] and Cat-II'

Catalyst	Ti supported[b)] (matom/g-cat.)	Mg supported[b)] (matom/g-cat.)	Cl supported[c)] (matom/g-cat.)	Cl/Ti
Cat-II	0.51	1.57	–	–
Cat-II'	0.46	0.003	0.95	2.1

a) The catalyst used in Run No. 5 in Tab. 1 was employed.
b) Measured by atomic absorption spectrophotometry.
c) Measured by elemental analysis.

From these results, a plausible mechanism of the active species may be depicted as follows.



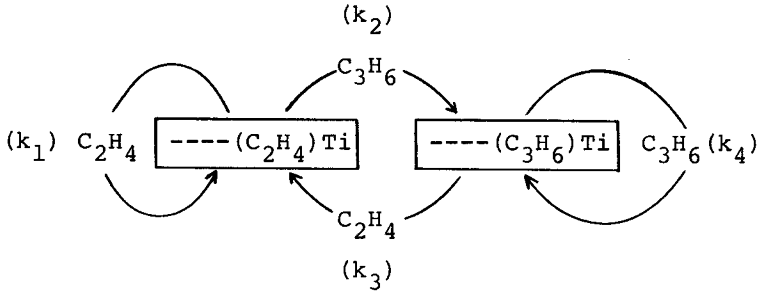
Copolymerization of ethylene with propylene was conducted in some detail using Cat-II. The results obtained (Tab. 3) were analyzed by using the same kinetic method reported previously (SOGA et al. 1982).

Table 3. Results of Ethylene-Propylene Copolymerization[a)]

Run No.	Propylene (mol %)	Activity (mol/g-Ti·h) Total	Ethylene	Propylene	Propylene in Copolymer[b)] (mol %)
1	34	26.1	19.7	6.4	25
2	45	20.4	13.9	6.5	32
3	53	19.0	10.6	8.4	44
4	63	14.3	7.3	7.0	49
5	70	11.2	5.1	6.1	54

a) Copolymerization was conducted at 40 °C for 45 min at an initial pressure of 40 cmHg over the $TiCl_4/MgCl_2/SiO_2$ catalyst (Cat-II) by using 0.05 mmol of $AlEt_3$ in 10 ml of n-heptane.
b) Measured by ^{13}C NMR.

The monomer reactivity ratios, r_1 $(=k_1/k_2)$, r_2 $(=k_4/k_3)$, were determined as $r_1=6$ and $r_2=1/6$, where k_1, k_2, k_3 and k_4 represent the rate constants of the following reactions.



The present monomer reactivity ratios are very close to those ($r_1=7$ and $r_2=1/7$) obtained with the SiO_2-supported $MgCl_2/TiCl_3$ catalyst combined with $AlEt_3$ (SOGA et al. 1982).

In conclusion, the SiO_2-supported $TiCl_4$ catalyst modified by $MgCl_2$ showed a very high activity for the random copolymerization of ethylene with propylene, and the monomer reactivity ratios with the present catalyst were found to be very close to those with the SiO_2-supported $MgCl_2/TiCl_3$ catalyst.

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