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# Polymerization of Propylene over Metal Oxides-Supported $TiCl_3$ Catalysts

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## Summary

Several metal oxides-supported $TiCl_3$ catalysts were prepared and propylene polymerization was conducted over them without cocatalysts. It was found that isotactic polymerization of propylene took place effectively over them.

## Introduction

We have recently found that isotactic polymerization of propylene takes place over titanium ion ($Ti^{3+}$ and $Ti^{4+}$) -exchanged Y-zeolite without organometallic compounds ( SOGA et al. 1979). The results obtained have led to the important conclusions that both $Ti^{3+}$ and $Ti^{4+}$ species are active and that neither Ti-alkyl bonds nor Cl ligands are necessarily essential for isotactic polymerization of propylene. However, the activities of these catalysts were very small owing to extremely small pores of Y-zeolite used as support. From this point of view a $SiO_2$-supported $TiCl_4$ catalyst was prepared by allowing $SiO_2$ to react with $TiCl_4$ in boiling n-heptane, followed by evacuation at 300 °C for 6 h. The catalyst, however, showed neither the ESR signal attributable to $Ti^{3+}$ nor the polymerization activity in the absence of cocatalysts (SOGA et al. in press). The $Ti^{4+}$ species, $\geq$Si-O-$TiCl_3$, in the $SiO_2$-supported catalyst is thus inactive for the polymerization because of the difficulty of coordination of propylene with the $Ti^{4+}$ species which is surrounded with three large Cl ligands. The catalyst was then reduced by $AlEt_2Cl$ in n-heptane at 65 °C for 1 h and the product was washed with plenty of n-heptane to remove the unreacted $AlEt_2Cl$. The reduced catalyst showed the ESR signal attributable to $Ti^{3+}$ as well as a considerable activity without cocatalysts. These results strongly suggest that the titanium consisting active species for the polymerization is $Ti^{3+}$ in case of the $SiO_2$-supported catalyst.

From this point of view, in this paper were prepared

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metal oxides-supported $TiCl_3$ catalysts and polymerization of propylene was conducted over them without cocatalysts.

## Experimental

Materials Research grade propylene and n-heptane (from Takachiho Chemical Co.) were purified according to the same procedures reported earlier (SOGA et al. 1977). Nitrogen of ultra high purity (from Nihon Sanso Co., 99.9989%) was further purified by passing through the molecular sieve 3A column cooled at -196 °C. The other chemicals (research grade) were also commercially obtained and used without further purification.

Preparation of the catalysts. The metal oxides-supported $TiCl_3$ catalysts were prepared by the following two methods.

[1] The mixture of the measured amounts of $TiCl_3$ (H-grade) and a metal oxide ($SiO_2$, $\gamma$-$Al_2O_3$ or MgO) was ground in a ball mill at room temperature for 45 h under a nitrogen atmosphere.

[2] In an aqueous solution of $TiCl_3$ at room temperature was immersed $SiO_2$. The solid product was separated by filtration, washed throughly with water, dried i. vac. at room temperature over night, and then evacuated at 100 - 450 °C for 3 h.

Polymerization procedures. In a 100 ml stainless steel reactor equipped with a magnetic stirrer were placed the measured amounts of the catalyst and n-heptane under a nitrogen atmosphere. The reactor was cooled by liquid nitrogen, degassed i. vac. and then 0.3 mol of propylene was introduced. The polymerizaton was terminated by adding plenty of a dilute hydrochloric acid solution in methanol. The polymer produced was extracted by hot o-dichlorobenzene, precipitated by adding plenty of methanol and dried i. vac. at room temperature.

Analytical procedures. The amounts of titanium contained in the catalysts were determined by atomic absorption spectrophotometry (Shimadzu AA-6105). The ESR spectrum was taken at -196 °C in a pyrex glass tube of 3 mm diameter on a JEOL JES-PE-IX ESR Spectrometer with 100 kc/sec field modulation. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) and $Mn^{2+}$ doped on MgO were used to determine the concentration of $Ti^{3+}$ and the g-value, respectively. The intrinsic viscosity of the polymer was measured at 135 °C in decaline and the molecular weight was calculated by the following equation (KINSINGER 1957).

$$[\eta] = 1.07 \times 10^{-4} [\bar{M}_W]^{0.80}$$

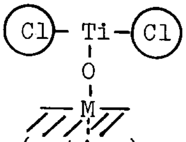
The isotacticity of the polymer was determined by the method of LUONGO (1960) with IR, from 995 and 974 $cm^{-1}$ bands.

## Results and Discussion

The mixture of $TiCl_3$ (H-grade) and each supporting material (metal oxide) which had been evacuated at 100 - 600 °C for 3 h was ground in a ball mill at room temperature for 45 h. A portion of each product was then evacuated at 300 °C for 3 h. Polymerization of propylene was conducted at 65 °C for 45 h by using them as catalyst without additives. The results obtained are shown in Table 1 together with some analytical data. The $\gamma$-$Al_2O_3$ and MgO-supported catalysts without evacuation at 300 °C gave only oligomers, which might be produced via a cationic mechanism. On the other hand, the other catalysts gave isotactic polypropylene with high molecular weights. The catalysts evacuated at 300 °C for 3 h showed considerably higher activities regardless of the metal oxides used as support. It may be considered that the reaction between surface hydroxyl groups of metal oxides and $TiCl_3$ (eq.1) partly takes place during the grinding procedure to give the active species, $\geqslant$M-O-$TiCl_2$.

$$\geqslant M\text{-}OH + TiCl_3 \longrightarrow \geqslant M\text{-}O\text{-}TiCl_2 + HCl\uparrow \qquad (1)$$

However most part of $TiCl_3$ may remain as small particles, which are inactive for the polymerization without cocatalysts because of the difficulty of coordination of propylene with the $Ti^{3+}$ species disturbed by Cl ligands. These species can schematically be shown as follows.



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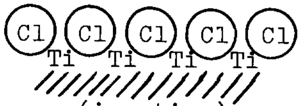

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The reaction (1) may also proceed to a certain degree during the evacuation process. This seems to be the main reason why the evacuated catalysts showed higher activities. The MgO used in the present study has only a small amount of surface hydroxyl groups (SOGA et al. 1979). Thus the MgO supported catalyst showed a very small activity. From such a point of view, another type of MgO having a considerable amount of surface hydroxyl groups was prepared by allowing the MgO to react with water at 300 °C for 12 h, followed by evacuation at 350 °C for 4 h. The catalyst with the use of the hydrated MgO showed a considerably high activity [ see c ) in Table

TABLE I

Results of propylene polymerization over the supported $TiCl_3$ catalystsa)

| | Catalyst | Evac. Temp.b) of Support (°C) | Evac. Temp. ofb) Supported Cat. (°C) | Polymer Yield (g/matom-Ti) | Ti supported (matom/g-cat) | I.I. (%) | $\bar{M}w$ ($x10^4$) |
|---|---|---|---|---|---|---|---|
| A | $SiO_2$-$TiCl_3$ | 100 | - | 2.71 | 1.20 | 65 | - |
| | " | 100 | 300 | 4.34 | 1.20 | 60 | 8.4 |
| | " | 600 | - | 0.50 | 0.95 | 43 | - |
| | " | 600 | 300 | 3.73 | 0.95 | 55 | 11 |
| | γ-$Al_2O_3$-$TiCl_3$ | 100 | - | 0.44 | 1.33 | oligomer | 0.20 |
| | " | 100 | 300 | 1.31 | 1.33 | 44 | 49 |
| | MgO-$TiCl_3$ | 350 | - | 0.060 | 1.63 | oligomer | - |
| | " | 350 | 300 | 0.041 | 1.63 | 59 | 24 |
| | MgO-$TiCl_3$c) | 350 | - | 0.26 | 1.65 | 70 | - |
| B | $SiO_2$-$TiCl_3$ | - | 100 | 0.180 | 1.82 | 73 | - |
| | " | - | 200 | 11.5 | 1.83 | 53 | - |
| | " | - | 300 | 14.0 | 1.85 | 50 | 16 |
| | " d) | - | 300 | 2.71 | 1.85 | - | - |
| | " | - | 450 | 0.270 | 1.92 | 48 | - |

A: prepared by the procedure[1] (see in the Text)

B: prepared by the procedure[2] (see in the Text)

a) Polymerization was conducted at 65 °C for 45 h by using 1.0 g of each catalyst, 5 ml of n-heptane and 0.3 mol of propylene in a 100 ml stainless steel reactor.

b) Each support or catalyst was evacuated for 3 h.

c) MgO allowed to react with water at 300 °C for 12 h in a stainless steel reactor before dehydration was also used as support.

d) Polymerization of ethylene was conducted at 65 °C for 0.5 h by using 1.0 g of catalyst, 5 ml of n-heptane and 0.2 mol of ethylene in the same reactor.

TABLE II

g-Value and line width of each catalyst[a)]

| Catalyst | Preparative method of cat. | Treatment of cat. | g-value | $\Delta H_{msl}$(gauss) |
|---|---|---|---|---|
| $TiCl_3$(H-grade) | A | - | 1.942 | 80 |
| $\gamma$-$Al_2O_3$-$TiCl_4$ | C | i.vac.[b)] | 1.942 | 85 |
| $\gamma$-$Al_2O_3$-$TiCl_3$ | A | i.vac.[b)] | 1.938 | 126 |
| $\gamma$-$Al_2O_3$-$TiCl_3$ | A | - | 1.941 | 107 |
| $Ti^{3+}$-Y zeolite | B | i.vac.[b)] | 1.945 | 35 |
| $SiO_2$-$TiCl_4$ | C | reduced by $AlEt_2Cl$ | 1.952 | 80 |
| $SiO_2$-$TiCl_3$ | A | i.vac.[b)] | 1.947 | 52 |
| $SiO_2$-$TiCl_3$ | A | - | 1.950 | 73 |
| $SiO_2$-$TiCl_3$(aq) | B | i.vac.[b)] | 1.947 | 72 |
| MgO-$TiCl_4$[c)] | C | - | 1.947(anisotropic signal) | |
| MgO-$TiCl_3$[c)] | A | i.vac.[b)] | 1.949 | 64 |
| MgO-$TiCl_3$[c)] | A | - | 1.943 | 106 |

A: prepared by the procedure[1] (see in the Text)

B: prepared by the procedure[2] (see in the Text)

C: $TiCl_4$ was allowed to react with the supporting materials (SOGA et al. in press).

a) The ESR spectrum was taken in a pyrex glass tube of 3 mm diameter at -196 °C on a JEOL-PE-IX ESR Spectrometer with 100 k/sec field modulation.

b) i.vac. at 300 °C for 3 h

c) MgO allowed to react with water at 300 °C for 12 h in a stainless steel reactor before dehydration was also used as support.

1].

Then several $SiO_2$-supported catalysts were prepared by immersing $SiO_2$ in an aqueous solution of $TiCl_3$, followed by evacuation at 100 - 450 °C for 3 h.[3] The typical results of propylene polymerization are shown in Table I together with some analytical data. The activity increased drastically, reached a maximum value at 300 °C and decreased to a great degree with increasing the evacuating temperature.

The low activities of the catalysts evacuated at 100 °C and 450 °C may mainly be attributed to the water left in the catalysts, and to the reduction of $Ti^{3+}$ to its lower valencies, respectively.

It should be noted that the activities of the catalysts prepared according to this procedure are considerably higher as compared with those of the catalysts prepared by grinding, which may owe to the higher dispersion of $TiCl_3$ on the supporting material.

In Table II are summarized the g-value as well as the line width of each catalyst used in the present or previous study. All the catalysts displayed the ESR signals attributed to $Ti^{3+}$ species, and the g-values of these catalysts were very close with one another.

The conclusion reached can be expressed as follows. The $Ti^{3+}$ species, $\equiv M\text{-}O\text{-}TiCl_2$ (M:metal used as support), formed by the reaction between $TiCl_3$ and surface hydroxyl groups of the supporting materials, with which propylene can easily by coordinated, are active for isotactic polymerization of propylene.

It may be considered, therefore, that the main role of the cocatalysts such as $AlEt_3$, $AlEt_2Cl$ etc. is to extract Cl ligands from the surface of $TiCl_3$ so that propylene can easily be coordinated with $Ti^{3+}$ species.

A precise study on the mechanism of propylene polymerization over these simple catalysts is presently being carried out and will be reported in another paper.

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