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Preparation of Highly Active Supported Catalysts for Producing Polypropylene with Less Content of Chloride

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Summary

Highly active supported catalysts for propylene polymerization have been prepared by treating the complexes of $TiCl_3 \cdot 3C_5H_5N$ and $MgCl_2 \cdot (THF)_x$ with $AlEt_2Cl$ in the presence of MgO, $Mg(OH)_2$ or SiO_2. Polypropylene with less content of chloride was produced over these catalysts combined with $AlEt_3$.

Introduction

Highly active supported catalysts for olefin polymerization continue to attract considerable attention and appear to be an object of study in many industrial and academic laboratories throughout the world. Detailed reviews of the supported catalysts have been presented by several authors (DIEDRICH 1975, WEISSERMEL et al. 1975, KAROL 1976, SIVARAM 1977, REICHERT 1977). Among these supported catalysts titanium chloride supported on $MgCl_2$ is apparently most active. In such a catalyst titanium chloride is highly dispersed on the $MgCl_2$ surface, so the activity per titanium atom is extremely high. But the activity per chloride atom, especially in the polymerization of propylene, is still considerably low. This disturbs the achievement of an economic process which requires no catalyst-removal step. Union Carbide has recently succeeded in preparing one of the ideal supported catalysts for polyethylene from tetravalent titanium compounds, $MgCl_2$ and metal oxides (KAROL 1979). The catalysts contain less amount of chloride and eliminate the need for a catalyst-removal in ethylene polymerization. However, they still show insufficient activity for the polymerization of propylene. In this paper is described a new preparative method of highly active supported catalysts for propylene polymerization.

Experimental

Materials Commercial extra pure grade n-heptane,

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pyridine and tetrahydrofuran (THF) were purified with the usual procedures. Extra pure grade $TiCl_3$ (H-grade), $MgCl_2$ (both from Toho Titanium Co. Ltd.), triethylaluminum (TEA) and diethylaluminum chloride (DEAC) were commercially obtained and used without further purification. Commercial extra pure grade ethyl benzoate (from Tokyo Kasei Co. Ltd.) was purified by passing through the molecular seive 3A column at room temperature. Research grade MgO (26.4 m^2/g), $Mg(OH)_2$ (43.1 m^2/g) (from Kanto Chemical Co. Ltd.) and SiO_2 (300 m^2/g) (from Fuji-Devison Chemical Co. Ltd.) were evacuated at 350 °C for 3 h immediately before use. Research grade propylene (from Takachiho Chemical Co. Ltd.) was purified according to the procedures reported earlier (SOGA et al. 1977). Nitrogen of ultra high purity (from Nihon Sanso Co. Ltd., 99.9995 % purity) was further purified by passing through the molecular sieve 3A column at -196 °C.

Preparation of the supported catalysts. $TiCl_3 \cdot 3C_5H_5N$ was prepared from the reaction of $TiCl_3$ with pyridine at room temperature. [$TiCl_3 \cdot 3C_5H_5N$ (391.5) Calc. C 45.98, H 3.83, N 10.73; Found C 45.64, H 3.96, N 10.74]. On the other hand, no specific complex between $MgCl_2$ and THF could be isolated. Therefore $MgCl_2 \cdot (THF)_x$ was prepared by dissolving $MgCl_2$ in THF followed by evacuation at room temperature for 5 h. Supported catalysts were usually prepared as follows. To 5 ml of n-heptane containing 4 mmol of DEAC were added the measured amounts of $TiCl_3 \cdot 3C_5H_5N$, $MgCl_2 \cdot (THF)_x$ and a supporting material under nitrogen. The mixture was kept standing with vigorous stirring for 20 h at room temperature. The precipitate was separated by filtration and washed with plenty of n-heptane.

Polymerization and analytical procedures. The polymerization of propylene was conducted with the same apparatus and procedures as described previously (SOGA et al. 1979). The amounts of titanium and magnesium contained in the supported catalysts were determined by atomic absorption spectrophotometry. The isotacticity of the polymer was determined by the method of LUONGO (1960) with IR, from 995 and 974 cm^{-1} bands. The surface areas of the supporting materials were measured by the BET method with nitrogen adsorption.

Results and Discussion

$TiCl_3$ is a crystalline solid which seems inconvenient for the production of highly dispersed supported catalysts. It is well known, however, that $TiCl_3$ easily forms a stable complex of $TiCl_3 \cdot 3C_5H_5N$ with pyridine and that the pyridine is easily removed from the complex by treating with Lewis acids. From this point of view we have succeeded in preparing the highly dispersed $MgCl_2$-supported $TiCl_3$ catalyst by treating $TiCl_3 \cdot 3C_5H_5N$ with DEAC in the presence of $MgCl_2$ (SOGA et al. to be published). The catalyst combined with TEA showed a marked activity for propylene polymerization. But the crude polymer obtained over the catalyst still contained a large amount of chloride atoms resulting from $MgCl_2$ used as support.

It is also known that $MgCl_2$ easily reacts with THF to give a complex of $MgCl_2 \cdot (THF)_x$. It may be expected that the THF ligands are also removed from the complex by treating with DEAC. The present study was aimed at the preparation of highly active catalysts which contain less amount of chloride by using the technique.

Several supported catalysts with various molar ratio of Mg/Ti were prepared by using MgO, $Mg(OH)_2$ and SiO_2 as support, and propylene polymerization was conducted at 65 °C for 15 min by using ca. 60 mg of each supported catalyst combined with TEA. The elemental analyses of the supported catalysts indicated the presence of a small amount of pyridine. Most of the residual pyridine is considered to be coordinated with the supporting materials (SOGA et al. to be published). The polymerization results obtained are shown in Table 1 together with some analytical data.

It should be quite noted that the specific activity (per Ti atom) drastically increased by co-existing only a small amount of $MgCl_2$. Thus, we have succeeded in producing polypropylene with much less content of chloride. Generally speaking, the specific activity increased drastically at first, passing through a maximum value and gradually decreased with an increase in the molar ratio of Mg/Ti (runs no. 3-6, 13-16 in Table 1). The decrease in the specific activity may result in the occlusion of $TiCl_3$ by $MgCl_2$. The activity also decreased slightly with increasing the amount of $TiCl_3$ supported (runs no. 6-9 in Table 1), which may reflect the dispersion of $TiCl_3$ on the surface.

Then several other types of supported catalysts were prepared for reference. The mixture of $TiCl_3 \cdot 3C_5H_5N$ (0.10 g), $MgCl_2 \cdot (THF)_x$ (0.10 g) and SiO_2 (1.0 g) in 10 ml of THF was kept standing at room temperature for 2 h with vigorous stirring in the absence of DEAC, followed by evacuation at 100 °C for 2 h to remove the residual THF. The product was separated into a pair of parts. One part was treated with DEAC while the other untreated. Then, similar catalysts were prepared by using 0.055 g of $TiCl_4$, 0.084 g of $MgCl_2$, 1.0 g of SiO_2 and 10 ml of THF according to the same procedures. Propylene polymerization was conducted by using them as catalyst (Table 2). The untreated catalysts (runs no. 17 and 19 in Table 2), which seem very close to the catalyst developed for ethylene polymerization by Union Carbide (KAROL 1979), showed very low activity for

Table 1. Polymerization Results over Various Supported Catalysts[a)]

Run No.	Support (50mg)	$TiCl_3 \cdot 3C_5H_5N$ (mg)	$MgCl_2 \cdot (THF)_x$ (mg)	Ethyl benzoate (mmol)	Ti supported (matom/ g-support)	Mg supported[b)] (matom/ g-support)	Activity (kg-pp/ g-Ti•h)	I.I. (%)
1	MgO	7	0	0	0.22	0	1.50	-
2	"	7	10	0	0.32	(1.18)	13.2	64
3	$Mg(OH)_2$	7	0	0	0.22	0	4.91	62
4	"	3	2	0	0.10	(0.24)	20.9	48
5	"	3	5	0	0.12	(0.60)	42.1[c)]	53
6	"	3	10	0	0.12	(1.18)	26.6	54
7	"	5	10	0	0.20	(1.18)	20.2	56
8	"	7	10	0	0.32	(1.18)	17.6	63
9	"	10	10	0	0.40	(1.18)	14.8	62
10	"	3	5	0.05	0.12	(0.60)	29.1	74
11	"	3	5	0.10	0.12	(0.60)	22.1	84
12	"	3	5	0.20	0.12	(0.60)	15.7	88
13	SiO_2	7	0	0	0.33	0	trace	-
14	"	7	2	0	0.28	0.24	5.44	58
15	"	7	5	0	0.32	0.60	14.1	59
16	"	7	10	0	0.32	1.18	13.4	63

(Continued)

a) Polymerization was conducted at 65 °C for 15 min with 0.5 mmol of TEA, 10 ml of n-heptane and 18 g of C_3H_6.

b) The value in each parenthesis was presumed from the one obtained in the case of SiO_2 (runs no. 14-16).

c) 6.25 kg-pp/g-Cl•h [For reference, in the case of the $TiCl_3 \cdot 3C_5H_5N$ (treated with DEAC) on $MgCl_2$-TEA system (SOGA et al. to be published, 122 kg-pp/g-Ti•h, 1.61 kg-pp/g-Cl•h]

Table 2. Polymerization Results over Other Types of Supported Catalysts[a]

Catalyst	Run No.	Treatment with DEAC	Ethyl benzoate (mmol)	Ti supported (matom/ g-support)	Mg supported (matom/ g-support)	Activity (kg-pp/ g-Ti•h)	I.I. (%)
$TiCl_3 \cdot 3C_5H_5N$ (0.10g), $MgCl_2 \cdot (THF)_x$ (0.10g), and SiO_2 (1.0g) in THF (10ml).	17	No	0	0.26	0.60	0.30	-
	18	Yes[b]	0	0.23	0.60	10.6	65
$TiCl_4$ (0.055g), $MgCl_2$ (0.084g) and SiO_2 (1.0g) in THF (10ml).	19	No	0	0.29	0.88	2.77	-
	20	Yes[b]	0	0.26	0.88	44.7[c]	51
	21	Yes[b]	0.2	0.26	0.88	21.7	79

a) Polymerization was conducted at 65 °C for 15 min with 50 mg of each catalyst, 0.5 mmol of TEA, 10 ml of n-heptane and 18 g of C_3H_6.

b) 50 mg of each catalyst was treated with 5 ml of n-heptane containing 4 mmol of DEAC for 20 h at room temperature under nitrogen. Then, the precipitate was separated and washed with 15 ml of n-heptane.

c) 5.31 kg-pp/g-Cl•h.

propylene polymerization. It is noteworthy that the activity was strikingly improved by the treatment with DEAC (runs no. 18 and 20 in Table 2).

The addition of ethyl benzoate to the present catalysts fairly raised the isotacticity of polypropylene keeping the activity considerably high (runs no. 10-12 in Table 1 and 21 in Table 2). However, the improvement of the isotacticity of polypropylene as well as the detailed mechanism of the polymerization are still left to be much studied in the future.

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