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Polymerization of Propylene with Highly Active $MgCl_2$-Supported $TiCl_3$ Catalyst

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Summary

The $MgCl_2$ supported $TiCl_3$ catalyst was prepared by grinding the mixture of $TiCl_3 \cdot 3Py$ and $MgCl_2$ in a ball mill. The catalyst was treated either i.vac. at 50-200°C or with alkylaluminum halides to remove the residual pyridine, and propylene polymerization was conducted at 65°C using the resulting catalysts combined with triethylaluminum. The catalyst treated with diethylaluminum chloride showed an extremely high activity for the polymerization.

Introduction

Recently, highly active supported transition metal catalysts combined with organometallic compounds are extensively used for the production of polyolefins. These supported catalysts continue to attract considerable attention and appear to be an object of study in many industrial and academic laboratories throughout the world. Numerous publications, particularly in the patent literature, describe new developments in this area of catalysis. Detailed reviews of the supported catalysts have been presented by several authors (DIEDRICH 1975, WEISSERMEL et al. 1975, KAROL et al. 1976, SIVARAM 1977, REICHERT 1977). Titanium chloride supported on magnesium chloride ($MgCl_2$) catalyst is apparently most active among these supported catalysts. As is well known, titanium tetrachloride ($TiCl_4$) exists in a liquid state at room temperature, whereas titanium trichloride ($TiCl_3$) is a crystalline solid which is inconvenient for the production of highly dispersed supported catalyst. This may be the main reason why most of the catalysts reported so far have been prepared with the use of $TiCl_4$. On the other hand, it is also well known that $TiCl_3$ easily forms a stable complex of $TiCl_3 \cdot 3C_5H_5N$ with pyridine.

From this point of view, in this study was

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prepared the $MgCl_2$-supported $TiCl_3$ catalyst from $MgCl_2$ and $TiCl_3 \cdot 3C_5H_5N$, and propylene polymerization was conducted over the catalyst.

Experimental

Materials Commercial extra pure grade n-heptane and pyridine were purified with the usual procedures. Extra pure grade $TiCl_3$ (from Toho Titanium Co. Ltd., H-grade), triethylaluminum (TEA), diethylaluminum chloride (DEAC) and ethyl benzoate were commercially obtained and used without further purification. $MgCl_2$ (from Toho Titanium Co. Ltd.) was evacuated at 150 °C for 50 h. Research grade propylene (from Takachiho Chemical Co.) was purified according to the same procedures reported earlier (SOGA et al. 1977). Nitrogen of ultra high purity (from Nihon Sanso Co. Ltd., 99.9989 % purity) was further purified by passing through the molecular sieve 3A column cooled at -196 °C.

Preparation of the $MgCl_2$-supported $TiCl_3$ catalyst. $TiCl_3 \cdot 3C_5H_5N$ 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]. The $MgCl_2$-supported $TiCl_3$ catalyst was prepared by grinding the mixture of this complex and $MgCl_2$ in a stainless steel ball mill under nitrogen at room temperature.

Polymerization procedures. In a 100 ml stainless steel reactor equipped with a magnetic stirrer were placed a measured amount of catalyst, TEA (or DEAC) and n-heptane under nitrogen. The reactor was cooled by liquid nitrogen, degassed i. vac. and then 0.80 mol of purified propylene was introduced. The polymerization was terminated by adding dilute hydrochloric acid solution in methanol. The polymer obtained was thoroughly washed with methanol and dried i. vac. at room temperature.

Analytical procedures. The amounts of pyridine and titanium contained in the supported catalyst were determined by elemental analysis and atomic absorption spectrophotometry (Shimadzu AA-6105), respectively. The molecular weight distribution of the polymer was measured at 135 °C by gel permeation chromatography (Waters Associates, Model 200) using four polystyrene gel columns [10^7, 10^6, 10^5, and 10^4 Å pore sizes] and o-dichlorobenzene as solvent. The flow rate of solvent was maintained at 1.0 ml/min. The calibration curve of the molecular weight was obtained on the basis of the universal calibration (GRUBISIC et al. 1967, OGAWA et al. 1972) with 10 standard samples of monodisperse polystyrene with molecular weights from 2100 to 2610000. The number and weight average molecular weights ($\overline{Mn}$, $\overline{Mw}$) were obtained by the standard procedure by using date at 1/2 count (2.5 ml elution volume). The isotacticity of the polymer was determined by the method of LUONGO (1960) with IR, from 995 and 974 cm^{-1} bands, obtained with a Hitachi EPI-G3 spectrometer. The surface area of $MgCl_2$ was measured by the BET method with nitrogen adsorption.

Results and Discussion

Several $MgCl_2$-supported $TiCl_3$ catalysts with different molar ratio of Mg/Ti were prepared by using $MgCl_2$ with the surface area of 10.3 m^2/g, and propylene polymerization was conducted at 65 °C for 2 h by using ca. 0.05 g of each catalyst combined with TEA or DEAC. The results obtained are shown in Table I. The catalyst gave a maximum activity at a molar ratio of Mg/Ti of 30 combined with TEA, but it was not so great.

It may be considered that the residual pyridine which strongly coordinates to the active species reduces the activity.

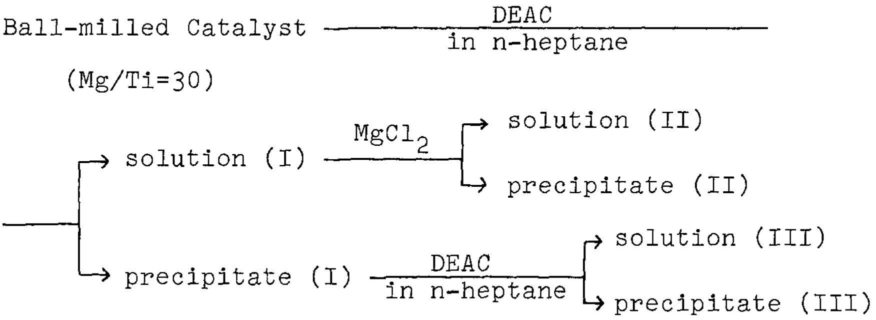
These catalysts were therefore evacuated at 50 - 200 °C to eliminate the residual pyridine. The results of the polymerization with the evacuated catalysts are also shown in Table I. Although appreciable amounts of the residual pyridine could be removed by the treatment, the activity decreased to a great extent in opposition to the expectation. Catalyst heating may result in the diffusion of titanium trichloride into the grain bulk (MAKHTARULIN et al. 1978).

Then the catalyst (Mg/Ti=30) was treated with alkylaluminum halides to eliminate pyridine chemically. In Table II are shown the results of the polymerization together with the analytical data of the catalyst. DEAC was the best among these alkylaluminum halides. With an increase in the contact time of the catalyst and DEAC, the amount of the residual pyridine decreased gradually and the activity increased drastically as a result.

The activities obtained with the use of similar catalysts prepared from $MgCl_2$ and $TiCl_3$ ($TiCl_4$) are also shown for reference.

It should be noted here that the amount of the residual titanium decreased at first and then gradually increased with an increase in the contact time of the catalyst and DEAC (Runs no. 1-6 in Table II). The result strongly implies that the titanium species once resolved in n-heptane was again chemisorbed on the catalyst surface.

To examine the propriety of this inference the following experiments were carried out.



The catalyst (Mg/Ti=30) was first treated with 2 mmol of DEAC in 5 ml of n-heptane at room temperature for 10 min. and the mixture was filtered under nitrogen. To the solution (I) was added 0.03 g of MgCl$_2$ and the mixture was stirred for 20 h at room temperature. Polymerization of propylene was then conducted by using the resulting precipitate (II) combined with TEA. As shown in Table II (Run no. 11), this system showed a considerably high activity. Thus, the above inference is considered plausible. On the other hand, the precipitate (I) was again treated with 2 mmol of DEAC in 5 ml of n-heptane for 20 h at room temperature. The final precipitate (III) was separated by filteration and thoroughly washed with n-heptane, which showed a very high activity (Run no. 12).

Both the isotacticity and the molecular weight distribution of the polymer obtained with the present catalysts were very close to those obtained over the catalyst prepared from MgCl$_2$ and TiCl$_3$.

Then a similar catalyst was prepared from TiCl$_3$·3C$_5$H$_5$N and MgCl$_2$ with a large surface area (43.3 m^2/g) (Mg/Ti=30). It was activated by treating with DEAC according to the similar procedures as shown above and propylene polymerization was conducted in some detail by using the final precipitate (III) combined with TEA and ethyl benzoate (for more details see Table III). The results obtained are shown in Table III. The catalyst showed an extremely high activity in the absence of ethyl benzoate. The addition of ethyl benzoate to the catalytic system caused a considerable increase in the isotacticity as well as a substantial decrease in the activity. However, the molecular weight distribution of the polymers obtained was hardly affected by the addition of ethyl benzoate.

The improvement of the isotacticity is now being tried out and the precise results will be reported in another paper.

TABLE I

Polymerization results over the $MgCl_2$-supported $TiCl_3$ catalysts evacuated at various temperatures[a)]

Run No.	Molar Ratio [Mg/Ti]	Evacuation Temp. [°C] (3h)	Activity [kg-pp/g-Ti·h]		Residual Pyridine[b)] [%]
			$AlEt_2Cl$	$AlEt_3$	
1	10	-	0.63	1.05	100
2	30	-	4.97	7.39	100
3	30	50	-	6.74	-
4	30	100	4.21	-	97
5	30	200	0.88	3.48	37
6	50	-	4.43	5.66	100
7	50	100	2.69	-	95
8	50	200	0.34	-	15
9	100	-	1.65	4.14	100
10	100	100	0.44	-	76
11	100	200	0.10	-	0

a) Polymerization was carried out at 65 °C for 2 h with ca. 0.05 g of each catalyst, 0.5 mmol of $AlEt_2Cl$ (or $AlEt_3$), 10 ml of n-heptane and 37 g of C_3H_6. $MgCl_2$ with the surface area of 10.3 m^2/g was used as support.

b) Estimated from the elemental analysis of the catalysts ($\frac{3\ \text{Pyridine}}{TiCl_3}$ x 100).

TABLE II

Polymerization results over the $MgCl_2$-supported $TiCl_3$ catalysts treated with Alkylaluminums a)

Run No.	Treating Time	Residual Ti [%]	Residual Pyridine [%]	Activity [kg-pp/g-Ti h]	I.I. [%]	$\overline{Mw}$ [x10^4]	Q [$\overline{Mw}/\overline{Mn}$]
1	10 min.	56	38	34.5	63		
2	30 min.	59	34	42.9	-		
3	1 h	65	32	42.1	-		
4	3 h	72	26	54.7	59		
5	20 h	80	21	64.4	58	29.1	13.0
6	100 h	84	15	63.5	57		
7	20 h b)	80	-	46.0	62		
8	20 h c)	80	-	61.1	-		
9	20 h d)	88	-	32.2	61		
10	20 h e)	92	-	8.9	-		
11	20 h f)	34	-	46.0	63		
12	10 min. + 20 h g)	39	14	132.1	55		
$TiCl_3$ supported on $MgCl_2$ (Mg/Ti=30)				1.5	61	33.0	13.1
$TiCl_4$ supported on $MgCl_2$ (Mg/Ti=44)				6.7	63		

a) Each catalyst (Ca. 0.03 g) was treated at room temperature (b) 65 °C) under a nitrogen atmosphere with 2 mmol (c) 10 mmol) of $AlEt_2Cl$ (d) $AlEtCl_2$, e) $AlEtI_2$) in 5 ml of n-heptane followed by washing with 15 ml of n-heptane. Polymerization was carried out at 65 °C for 1 h with 0.5 mmol of $AlEt_3$, 10 ml of n-heptane and 37 g of C_3H_6. f) Precipitate (II) and g) Precipitate (III) were used as catalyst (for more details see in the Text).

TABLE III

Polymerization results over the $MgCl_2$-supported $TiCl_3$ catalysts[a)]

Run No.	$AlEt_3$ [mmol]	Etyl benzoate [mmol]	Activity [kg-pp/g-Ti·h]	I.I. [%]	$\overline{Mw}$ [$x10^4$]	Q [$\overline{Mw}/\overline{Mn}$]
1	0.1	0	780	59		
2	0.1	0.025	3	-		
3	0.1	0.05	2	-		
4	0.3	0.025	86	74		
5	0.4	0.05	131	83		
6	0.5	0	650	58	40.2	6.3
7	0.5	0.025	162	73	43.1	7.3
8	0.5	0.05	295	87	53.4	7.1
9	0.6	0.025	175	72		
10	0.6	0.05	162	73		
11	0.8	0.05	149	68		
12	1.0	0.025	98	63		
13	1.0	0.05	119	66		
14	1.0	0.1	77	68		
15	2.5	0	100	52		

a) Each catalyst (ca. 0.01 g) was treated at room temperature with 2 mmol of $AlEt_2Cl$ in 5 ml of n-heptane for 10 min. Then the precipitate was filtrated and treated with 0.7 mmol of $AlEt_2Cl$ in 1.7 ml of n-heptane for 20 h followed by washing 15 ml of n-heptane (residual Ti was 19 %). Polymerization was carried out at 65 °C for 15 min. with 10 ml of n-heptane and 37 g of C_3H_6. $MgCl_2$ with the surface area of 43.3 m^2/g was used as support.

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