

Catalysts

Highly Active MgO-Supported TiCl₄ Catalyst for the Ethylene Polymerization

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SUMMARY

The MgO-supported TiCl₄ catalysts prepared by heating MgO with TiCl₄ showed a high activity for the ethylene polymerization in combination with Et₃Al or i-Bu₃Al. In these highly active catalysts, it has been shown that MgCl₂ is formed in the MgO-TiCl₄ reaction and is considered to contribute to the enhancement of the activity of the catalysts.

INTRODUCTION

Since the discovery of the Ziegler-catalyst, a great deal of studies have been carried out in the field of supported catalyst and a number of the great successes have been accomplished with the development of highly active catalyst systems, especially, by the use of MgCl₂ as a support(1). Not only MgCl₂, but also MgO has already been known to be effective to enhance the activity in the polymerization of olefins(2,3,4). A.Simon et. al. studied on the MgO-supported TiCl₄ catalyst, and reported that "coordinatively unsaturated" O²⁻ sites on MgO were possible precursors of the active centers in the polymerization(5). A.A.Baulin et.al. reported that MgCl₂ was found in the MgO-supported TiCl₄ catalyst from the X-ray analysis data(3).

In this paper, the analysis of the entitled catalyst and it's activity in the ethylene polymerization are discussed.

EXPERIMENTAL

Materials

TiCl₄ (from Osaka Titanium Co., Japan), Et₃Al (from Nippon Alkyl-Aluminium Co., Japan) and i-Bu₃Al (from Nippon Alkyl-Aluminium Co., Japan) were used without further purification. Decane and hexane were used after nitrogen bubbling for 2 h. Three samples of MgO having different amounts of surface hydroxyl groups (from Kyowa Kagaku Kogyo Co., Japan) were used after drying at 120°C for 72 h in vacuo. Ethylene (from Mitsui Petrochemical Co., Japan) had a purity of over 99.9 %.

Preparation of the MgO-supported TiCl₄ catalyst

One hundred milliliters of TiCl₄ and 10 g of MgO were put in a 400 ml flask equipped with a stirrer under nitrogen, and the mixture was stirred at the predetermined temperature for 1.5 h. Subsequently, the solid product (catalyst) was separated by the filtration at the reaction temperature, washed with hexane repeatedly to remove the unsupported TiCl₄ and dried in vacuo at room temperature for 2 h. The amount of Ti, Mg and Cl contained in the catalyst were determined by the colorimetric analysis, the atomic absorption one and the titrimetric one by the use of AgNO₃, respectively. The crystal structure of the catalyst was examined by X-ray analysis.

Polymerization

(a) The predetermined amount of the catalyst, Et_3Al and 500 ml of decane were added to 1 l of a glass reactor equipped with a stirrer under nitrogen, and then ethylene was introduced. The polymerization was carried out under the ambient pressure at 70°C for 1 h. (b) The predetermined amount of the catalyst, $\text{i-Bu}_3\text{Al}$ and 1 l of decane were added to 2 l of a stainless steel reactor equipped with a stirrer under nitrogen, and then 5 $\text{kg/cm}^2\text{G}$ of hydrogen and 5 $\text{kg/cm}^2\text{G}$ of ethylene were introduced. The polymerization was carried out under 10 $\text{kg/cm}^2\text{G}$ of total pressure at 90°C for 2 h (Ethylene was supplied to keep the total pressure at 10 $\text{kg/cm}^2\text{G}$). The polymer produced was filtrated, washed with hexane and vacuum-dried at 80 °C for 12 h.

Measurement of the surface hydroxyl groups on MgO

Five grams of MgO and 50 ml of decane were added under nitrogen to a 100 ml flask connected with a gas burette (250 ml), and heated to 130°C with stirring by a magnetic stirrer. Subsequently, 10 ml of Et_3Al was added dropwise, the evolution of ethane took place by the similar equation to $\text{SiO}_2(6)$, i.e., $-\text{Mg-OH} + \text{Et}_3\text{Al} \longrightarrow -\text{Mg-O-Al-Et}_2 + \text{EtH}$. The amount of the surface hydroxyl groups was calculated from the combined amount of ethane trapped in a gas burette and dissolved in decane. The ethane had a purity of over 97 %.

Extraction of the supported catalyst by ethyl alcohol

A sample of Catalyst No.5 (2.56 g) in Table 3 was put in 10 ml of ethyl alcohol at room temperature and stirred for 2 h, the supernatant was used for analysis.

RESULTS AND DISCUSSION

In Table 1, the activity (in g of polymer/mmol of Ti) of the MgO-supported TiCl_4 catalyst in ethylene polymerization is compared with the two systems (together with $\text{i-Bu}_3\text{Al}$), one is TiCl_4 and the other is a mixture of TiCl_4 with MgO without any pre-treatment. The latter two unsupported catalysts showed a low activity. On the other hand, the MgO-supported TiCl_4 catalyst was 100 times as high in activity as the unsupported catalysts. Thus, it is clear that supporting of TiCl_4 on MgO is effective for the enhancement of the activity.

Table 1 Activity in the ethylene polymerization

Catalyst	Activity (g of polymer/mmol of Ti)
TiCl_4	10
$\text{TiCl}_4 + \text{MgO}$ 1)	20
$\text{TiCl}_4 / \text{MgO}$ 2)	2700

1) 10 g of MgO and 5.4 mmol of TiCl_4 were mixed in 50 ml of decane at room temperature just before use.

2) MgO-supported TiCl_4 catalyst, Cat.No.3 in Table 2. Polymerization conditions; 90°C for 2 h under 5 $\text{kg/cm}^2\text{G}$ of H_2 and 10 $\text{kg/cm}^2\text{G}$ of total pressure, 0.5 mmol of Ti (0.1 mmol in 2)) and 3.0 mmol of $\text{i-Bu}_3\text{Al}$ in 1 l of decane.

In order to know what kinds of the reaction had occurred and why the activity had increased, the following examinations were carried out.

At first, the effect of the reaction temperature was examined. Table 2 shows that the catalysts prepared at higher temperature (hereinafter, called "H-catalyst") contained the higher amount of Ti and Cl fixed in comparison with those prepared at lower temperature (hereinafter, called

Table 2 Effect of the reaction temperature on the activity and the amount of Ti and Cl fixed

Cat.No.	Temperature (°C)	Ti (mmol/g-cat)	Cl (mmol/g-cat)	Cl/Ti	Activity (g of polymer/mmol of Ti)
1	0	0.35	1.52	4.3	390
2	20	0.38	1.44	3.8	470
3	100	0.54	4.11	7.6	2700
4	130	0.61	7.14	11.7	3100

MgO having surface hydroxyl groups of 1.32 mmol/g-MgO was used. Polymerization conditions ; 90°C for 2 h under 5 kg/cm²G of H₂ and 10 kg/cm²G of total pressure, 0.1 mmol of Ti and 3.0 mmol of i-Bu₃Al in 1 l of decane.

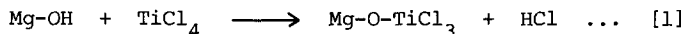
Table 3 Effect of the amount of surface hydroxyl group on the activity and the amount of Ti and Cl fixed

Cat.No.	-OH (meq/g-MgO)	Ti (mmol/g-cat)	Cl (mmol/g-cat)	Cl/Ti	Activity (g of polymer/mmol of Ti)
5	0.41	0.14	2.11	15.1	1100
6	0.60	0.22	3.15	14.3	1130
4	1.32	0.61	7.14	11.7	1080

Catalyst prepared at 130°C. Polymerization conditions ; 70°C for 1 h under the ambient pressure of ethylene, 0.05 mmol of Ti and 0.5 mmol of Et₃Al in 500 ml of decane.

"L-catalyst"), especially, the amount of Cl fixed. The Cl/Ti ratio was 7-12 in H-catalysts whereas it was 4 in L-catalysts. In the ethylene polymerization, H-catalysts were 5 times as high in activity as L-catalysts. Accordingly, the nature of the active sites seems to have been changed quite significantly by the change of the reaction temperature, and the higher Cl/Ti ratio (7-12) is considered to be very important for the higher activity.

Previous paper(5,7) proposed that TiCl_4 was fixed on MgO by the reaction with the surface hydroxyl group, as eq.[1].



Therefore, the effect of the amount of surface hydroxyl groups of MgO was examined (Table 3). The catalyst was prepared at 130°C. The higher the amount of the surface hydroxyl groups of MgO was, the higher the amount of Ti and Cl fixed was. However, there was no proportional relation between the former and the latter. The activity was almost same with three MgO samples employed here. According to eq.[1], the Cl/Ti ratio should not exceed 3 (the Cl/Ti ratio is less than 4, even though the adsorption of TiCl_4 and HCl on MgO were considered). In our results as shown Tables 2 and 3, as for the lower activity L-catalyst, the above is acceptable, however, as for H-catalyst, the Cl/Ti ratios were more than 7, and the Cl/OH ratios were 5.1-5.4. Therefore, it should be considered that not only the simple reaction as eq.[1], but also the other reactions, namely, the chlorination reaction of MgO, proceeded in the reaction of TiCl_4 and MgO at higher temperature.

Then, the reaction products for the H-catalyst were examined. After the reaction of TiCl_4 and MgO at 130°C, the filtrate was separated by filtration at 130°C, which was cooled to room temperature to produce yellow precipitation. The contents of Ti and Cl in the precipitate were found to be 35.2 and 49.1 wt%, respectively (Table 4), being consistent with those of TiOCl_2 (Ti 35.6 and Cl 52.6 wt%).

Table 4 Composition of the precipitate separated from the filtrate

	Ti (wt%)	Cl (wt%)
Found	35.2	49.1
Calcd.*	35.6	52.6

* Calculated as TiOCl_2

Next, H-catalyst was put into ethyl alcohol at room temperature and stirred for 2 h to extract the soluble components. In the ethyl alcohol solution, Mg, Cl and Ti were detected (Table 5). The Table shows that 90 % of Ti and Cl atoms and 10 % of Mg atoms in H-catalyst could be extracted.

Table 5 Components extracted by ethyl alcohol

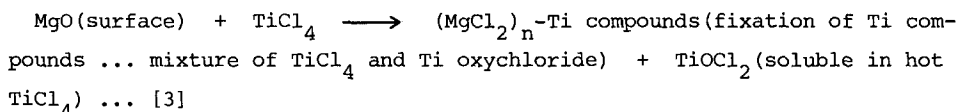
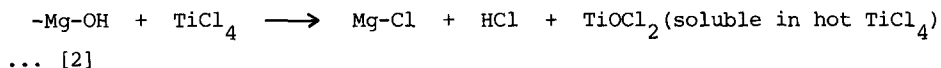
Mg	Cl	Ti
2.10	4.96	0.33

Unit ; $\text{mmol}/10 \text{ ml}$ of ethyl alcohol

Extraction conditions ; see Experimental

The Cl/Mg ratio is about 2, which indicates the production of MgCl_2 . The amount of MgCl_2 shows that about 10 mole % of MgO was converted to MgCl_2 in the H-catalyst preparation.

From these results, the reaction of TiCl_4 and MgO can be expressed in the following way in addition to eq.[1].



The formation of MgCl_2 in the catalyst preparation reaction (eq. [3]) is consistent with the results reported by A.A. Baulin et al. (3) although the presence of the crystalline MgCl_2 reported by them was not confirmed in our X-ray analysis.

In addition, Table 3 shows that the higher amount of Cl atoms fixed resulted in the higher amount of Ti atoms fixed. This fact suggests that in H-catalyst, TiCl_4 was supported on MgCl_2 rather than MgO as shown eq. [3].

MgCl_2 -supported TiCl_4 catalyst has already been reported to be highly active for olefin polymerization (8) and TiCl_4 is considered to be fixed in the matrix of MgCl_2 (8). As mentioned before, the catalysts prepared at lower temperature, in which titanium chloride may be fixed by eq. [1], showed low activity. On the other hand, the catalysts prepared at higher temperature, in which the chlorination reaction took place and titanium compounds may be fixed in MgCl_2 by eq. [3] in addition to eq. [1], showed high activity. Therefore, the high activity of the MgO -supported TiCl_4 catalyst in this report is attributable to the fixation of titanium compounds in the matrix of MgCl_2 formed by the reaction of MgO with TiCl_4 .

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