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Catalysts

Highly Active MgO-Supported $TiCl_4$ Catalyst for the Ethylene Polymerization

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SUMMARY

The MgO-supported $TiCl_4$ catalysts prepared by heating MgO with $TiCl_4$ showed a high activity for the ethylene polymerization in combination with Et_3Al or $i\text{-}Bu_3Al$. In these highly active catalysts, it has been shown that $MgCl_2$ is formed in the MgO-$TiCl_4$ 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 $MgCl_2$ as a support(1). Not only $MgCl_2$, 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 $TiCl_4$ catalyst, and reported that "coordinatively unsaturated" O^{2-} sites on MgO were possible precursors of the active centers in the polymerization(5). A.A.Baulin et.al. reported that $MgCl_2$ was found in the MgO-supported $TiCl_4$ 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

$TiCl_4$(from Osaka Titanium Co., Japan), Et_3Al(from Nippon Alkyl-Aluminium Co., Japan) and $i\text{-}Bu_3Al$(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 Pitrochemical Co., Japan) had a purity of over 99.9 %.

Preparation of the MgO-supported $TiCl_4$ catalyst

One hundred mililiters of $TiCl_4$ 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 $TiCl_4$ 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 $AgNO_3$, 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, $i\text{-}Bu_3Al$ and 1 *l* of decane were added to 2 *l* of a stainless steel reactor equipped with a stirrer under nitrogen, and then 5 kg/cm^2G of hydrogen and 5 kg/cm^2G of ethylene were introduced. The polymerization was carried out under 10 kg/cm^2G of total pressure at 90°C for 2 h(Ethylene was supplied to keep the total pressure at 10 kg/cm^2G). The polymer produced was filtrated, washed with hexane and vacuum-dried at 80 °C for 12 h.

Measurment 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 burrete(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 SiO_2(6), i.e., $\text{-Mg-OH} + Et_3Al \longrightarrow \text{-Mg-O-Al-}Et_2 + EtH$. The amount of the surface hydroxyl groups was calculated from the combined amount of ethane trapped in a gas burrete 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 $i\text{-}Bu_3Al$), 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
$TiCl_4$ + MgO 1)	20
$TiCl_4$ / 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 kg/cm^2G of H_2 and 10 kg/cm^2G of total pressure, 0.5 *mmol* of Ti(0.1 *mmol* in 2)) and 3.0 *mmol* of $i\text{-}Bu_3Al$ in 1 *l* of decane.

In order to know what kinds of the reaction had occured 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/cm^2G of H_2 and 10 kg/cm^2G of total pressure, 0.1 *mmol* of Ti and 3.0 *mmol* of i-Bu_3Al 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 Et_3Al 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].

$$\text{Mg-OH} + TiCl_4 \longrightarrow \text{Mg-O-}TiCl_3 + HCl \quad \ldots \quad [1]$$

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

* Caluclated 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 ; *mmol*/10 *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].

-Mg-OH + $TiCl_4$ $\longrightarrow$ Mg-Cl + HCl + $TiOCl_2$(soluble in hot $TiCl_4$) ... [2]

MgO(surface) + $TiCl_4$ $\longrightarrow$ $(MgCl_2)_n$-Ti compounds(fixation of Ti compounds ... mixture of $TiCl_4$ and Ti oxychloride) + $TiOCl_2$(soluble in hot $TiCl_4$) ... [3]

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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