

Catalysts

MgCl₂ Supported Titanium Catalyst Prepared by Mechanical Pulverization

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Summary

MgCl₂ supported titanium catalysts were prepared by mechanical pulverization of MgCl₂ with titanium compounds using two types of machines, rotatory mill and vibratory mill. Both methods gave substantially the same results, although vibratory mill much saved the milling time. The nature of the fixed titanium compounds was not homogeneous, and the titanium compounds fixed at an earlier stage of milling, which could be located at exposed "active" edge positions of MgCl₂ particles, showed higher activity in ethylene polymerization. On the other hand, those fixed at the later stage showed lower activity and caused reaggregation of the particles. Furthermore, chlorine-free titanate compounds, Ti(OBu)₄ and Ti(OEt)₄, also could be fixed on MgCl₂, which showed high activity in ethylene polymerization.

Introduction

It is well known that the activity of MgCl₂ supported titanium catalysts is about 100 times as high as that of the non-supported catalysts in olefin polymerization. (1) In the previous paper (2), we reported the catalysts prepared by milling of MgCl₂ with TiCl₄ using a rotatory mill. Galli et al. (3) reported the above catalysts prepared by using a more powerful vibratory mill. This paper reports investigations on the milled MgCl₂-TiCl₄ catalysts to obtain more detailed knowledge on these catalysts by using the above two types of milling machines, and also on the milled MgCl₂-Ti(OR)₄ catalysts in which the titanium compounds have no chlorine atoms.

Experimental

Preparation of supported catalyst

1) Rotatory mill method; Twenty grams of MgCl₂ and the predetermined amount of titanium compounds were put into a jar (capacity 0.8 l.) and milled at 120 r.p.m.. A rotatory mill of Yamato Scientific Co. LTD. (Japan) was employed. The jar was filled up to 50 % of the volume by the steel balls (diameter 15.8 mm). Working temperature was at 20 °C. As a control, MgCl₂ was milled in the absence of TiCl₄.

2) Vibratory mill method; A vibratory mill made by Yasukawa Electric Co. LTD. (Japan) (1750 cycles/min., total amplitude oscillation of 2.9 mm) was employed. A jar (capacity 0.8 l.) was filled up to 80 % of its volume by the steel balls (diameter 15.8 mm) and was loaded with 20 grams of MgCl₂ and the predetermined amount of titanium compounds. The mill was operated² at a gravity of 7. Temperature of the outside wall of the jar was maintained at 20 °C by water cooling system. The obtained milled products from 1) and 2) were washed with hexane several times and dried in vacuo.

3) Treatment of pre-milled $MgCl_2$ with excess amount of $TiCl_4$; Ten grams of $MgCl_2$, milled for 150 hrs with rotatory mill was suspended in 100 ml of $TiCl_4$ for 3 hrs at 20 °C with stirring, and the solids were separated and washed with hexane.

The determination of Ti content by colorimetric method, the measurement of specific surface area by BET and XRD analysis were performed on the above milled products.

Ethylene polymerization

1) Atmospheric pressure polymerization: Polymerization was carried out in a 1-l glass flask. Under nitrogen 0.5 l of decane, 0.5 mmol of $AlEt_3$, and the supported catalyst containing 0.01 mmol of titanium were introduced, and ethylene was fed 1 hr at 80 °C.

2) Pressurized polymerization: Polymerization was carried out in a 2-l autoclave with a magnetic stirrer. One liter of decane, 1 mmol of $AlEt_3$ and the supported catalyst containing 0.02 mmol of titanium were introduced into the autoclave. Hydrogen and ethylene, at the partial pressures of 4 and 4 Kg/cm^2 , respectively, were supplied. Ethylene was continuously fed to maintain the total pressure of 8 Kg/cm^2 for 2 hrs at 80 °C.

Results and Discussion

Catalyst preparation by rotatory mill

Fig. 1 shows the correlation between the milling time and specific surface area of the milled products. The rate of the increase of specific surface area depends considerably upon the $TiCl_4/MgCl_2$ ratio at the earlier stage of milling. The fastest rate was obtained at the Ti/Mg ratio of 1.2, the second was at the ratio of 0 ($MgCl_2$ alone milling), and the slowest was at the ratio of 2.0. This result may be explained as follows, i.e., in the first case, the fixed $TiCl_4$ in the matrix of $MgCl_2$ worked as a sort of the wedge to accelerate the destruction of the $MgCl_2$ matrix and the increase of specific surface area, on the other hand, in the third case, excess of the liquid $TiCl_4$ acted as a lubricant to cause slippage to decrease milling efficiency. Three milled products attained almost the same maximum values of specific surface area, 90-110 m^2/g , although there were very large differences in the required time to attain them. (Ti/Mg=1.2, 20 hrs, Ti/Mg=2.0, 100 hrs) The presence of $TiCl_4$ in the milling process gave a maximum peak of specific surface area (Fig. 1). Thus, $TiCl_4$ caused the decrease of specific surface area after maximum value.

Fig. 2 shows the correlation between the milling time and the ratio of half-peak-width values of (003) of $MgCl_2$ crystal (milled products/raw $MgCl_2$). As for the rate of the increase of half-peak-width values at the earlier stage of milling, in this case also, the same effect by the $TiCl_4/MgCl_2$ ratio could be seen, namely the fastest one was at the Ti/Mg ratio of 1.2 and the slowest was at the ratio of 2.0. However, there could be seen no maximum peaks in this case. Half-peak-width values were not always correlated to those of specific surface area. In the later stage of milling, as for the milled products with $TiCl_4$, the former was kept to be constant, while the latter decreased. From these facts, the behavior of the fixed $TiCl_4$ can be best explained by assuming that they caused reaggregation of the particles not to accompany the enlargement of the crystalline size of $MgCl_2$. Reaggregation would be caused by the fixed $TiCl_4$ through the chlorine coordinations into the coordinatively unsaturated Cl-vacant position in the adjacent particles.

Fig. 3 shows the correlation between the milling time and the contents of the titanium atoms fixed on $MgCl_2$. The titanium content

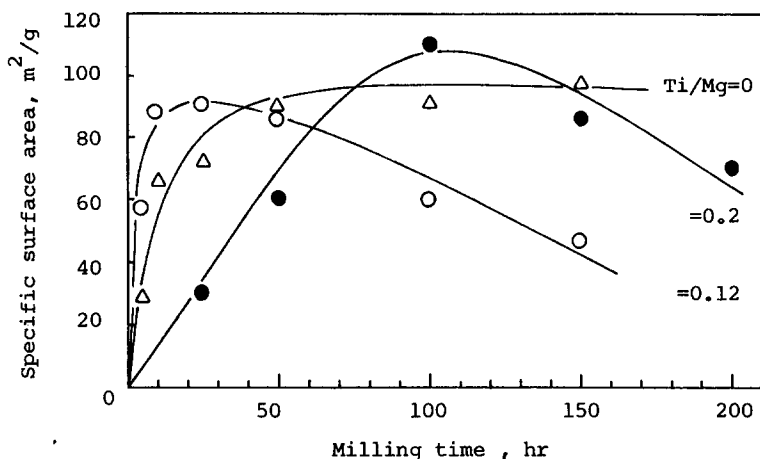


Fig. 1. Milling time vs specific surface area (Rotatory mill method)

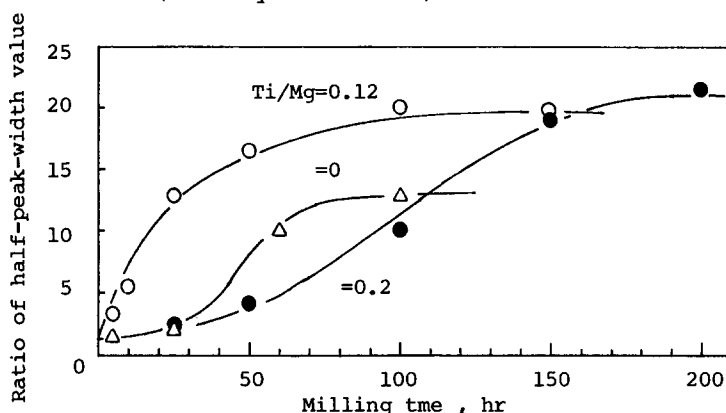


Fig. 2. Milling time vs the ratio of half-peak-width value (Rotatory mill method)

increased very rapidly during the earlier stage of milling and reached to the maximum values which were 80% of the added TiCl_4 . The time to attain the maximum content correlated to the corresponding time in half-peak-width values.

Catalyst preparation by vibratory mill

Fig. 4 shows the correlation between the milling time and specific surface area of the products obtained by milling of MgCl_2 with TiCl_4 using vibratory mill. In comparison with the case of rotatory mill the large difference was observed only in specific surface area which increased very quickly owing to the higher milling efficiency of vibratory mill. However, each of the maximum value was almost the same as the corresponding value of rotatory mill method, and the similar decrease after the maximum value was also seen. Moreover, Fig. 5 shows that the maximum titanium content in the catalysts was also almost the same as the corresponding value of rotatory mill method, although the time to attain the maximum content was much shortened. Therefore, we concluded that both methods gave substantially the same results, although vibratory mill could save milling time.

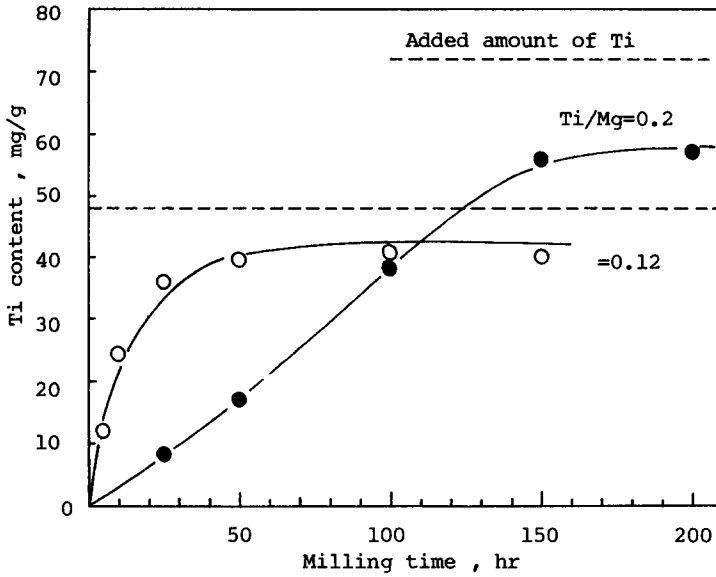


Fig. 3. Milling time vs Ti content
(Rotatory mill method)

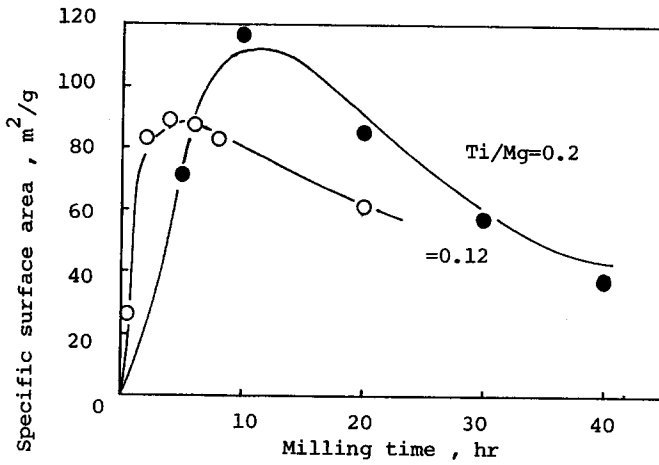


Fig. 4. Milling time vs specific surface area
(Vibratory mill method)

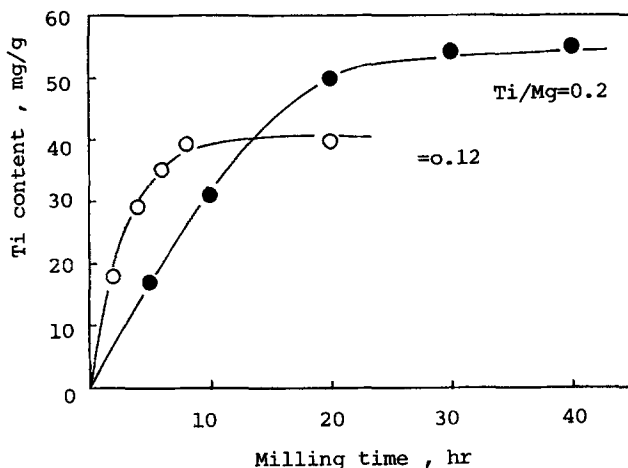


Fig. 5. Milling time vs Ti content
(Vibratory mill method)

Ethylene polymerization

In Figures 6 and 7, the catalyst activity (ethylene polymerization under atmospheric pressure) is plotted against the titanium contents with the two groups of supported catalysts prepared by rotatory and vibratory methods, respectively. In both figures, the catalysts having lower titanium content showed the much higher activity per unit titanium atom. These results show that TiCl_4 was fixed on MgCl_2 in a heterogeneous way, and it is supposed that those fixed preferentially in exposed position at the earlier stage of milling has higher activity. According to the increase of the amount of the fixed TiCl_4 , some portion of TiCl_4 was hidden inside of the catalyst particles by reaggregation, and consequently the catalyst activity per unit titanium atom rapidly decreased. This tendency was particularly remarkable in vibratory mill method, and the activity of the catalyst having the titanium content more than 30 mg of titanium atoms per one gram of the catalyst was almost a half of the activity of such catalyst by rotatory mill method. It is to be noted in Table 1, however, that the results in pressurized polymerization are different from those in atmospheric pressure polymerization. In pressurized polymerization, there were no significant differences in the respective activities of the catalysts prepared with two milling methods, having the similar titanium content (35-55 mg-Ti/g-cat). It may be assumed that the lower activity of the catalysts prepared with vibratory mill in atmospheric pressure polymerizations had been caused by heavier reaggregation of the catalyst particles and that the formation of the much higher amount of the polymer in the catalyst particles in pressurized polymerizations caused the considerable disintegration of the reaggregated catalyst particles to cancel the negative effect by reaggregation.

Thus, it is concluded also from the view point of catalyst activity that the two groups of catalysts prepared by rotatory and vibratory mill methods are substantially the same in nature. However, even in pressurized polymerizations, the catalysts having the lower titanium content still showed higher activity (the heterogeneity of the nature of the fixed TiCl_4).

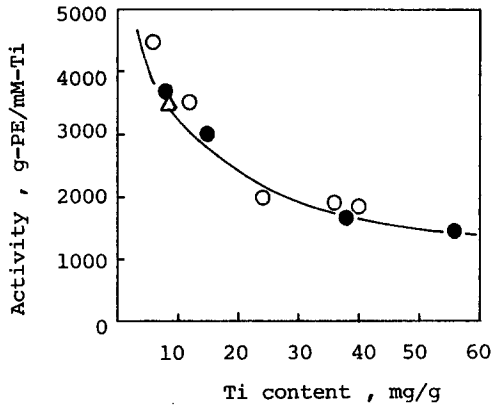


Fig. 6. Ti content vs activity
-rotatory milling system-

(Δ: Catalyst was prepared by the treatment of the pre-milled $MgCl_2$ with the large amount of $TiCl_4$)

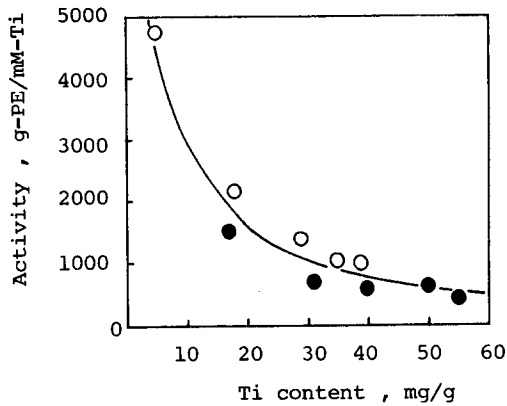


Fig. 7. Ti content vs activity
-vibratory milling system-

Table 1. Ethylene Polymerization Activities of Catalysts Obtained by Two milling Methods

No.	Milling conditions		Ti contents		Activities 3)	
	Methods	$TiCl_4/MgCl_2$	Times	mg/g	(A)	(B)
		M/M	hr		g-PE/mM-Ti	
1	R ¹⁾	0.1	25	34	1890	9190
2	"	0.2	150	56	1410	6440
3	V ²⁾	0.1	6	35	990	9460
4	"	0.2	40	55	550	5290

1) Rotatory mill method 2) Vibratory mill method

3) A) Atmospheric pressure polymn. B) Pressurized polymn.

Next, the fixation of $TiCl_4$ by simple mixing of the pre-milled $MgCl_2$ (without $TiCl_4$) with a large amount of liquid $TiCl_4$ was tried. The pre-milled $MgCl_2$ having $100\text{ m}^2/\text{g}$ of specific surface area was merely suspended in $TiCl_4$ at $20\text{ }^\circ\text{C}$, and separated. In one gram of the obtained solid catalyst by the above simple treatment, 8 mg of the titanium atoms were contained. In this catalyst, it is considered that $TiCl_4$ was fixed mostly on the exposed "active" edge positions of $MgCl_2$ particles produced by milling. The activity of this catalyst in ethylene polymerization was very high and it could be plotted on the same line of those of the catalysts obtained in $MgCl_2$ - $TiCl_4$ milling system at an earlier stage. (Fig. 6) These results strongly suggest that $TiCl_4$ fixed at an earlier stage of milling was located preferentially at exposed positions of particles to give higher activity.

$MgCl_2$ - $Ti(OR)_4$ supported catalyst

Chlorine-free titanate compounds, $Ti(OBu)_4$ and $Ti(OEt)_4$, were milled with $MgCl_2$ in the same way as $TiCl_4$. Both titanates could be fixed on $MgCl_2$, and the activities of those catalysts combined with $AlEt_3$ in ethylene polymerization were comparable to those of the $TiCl_4$ based supported catalyst systems. (Table 2) The obtained polyethylene had higher molecular weight. (Melt Flow Rate 2-7) The catalyst system consisting of chlorine-free titanate and $AlEt_3$ is known to produce mostly oligomers such as butene-1 in ethylene polymerization, whereas chlorine containing titanate produce high polymers. Although the manner of the fixation of $Ti(OR)_4$ compounds on $MgCl_2$ is not clear, the above results suggest that in this supported catalyst, chlorine atoms of $MgCl_2$ participated as the ligands surrounding Ti atom fixed on $MgCl_2$.

Table 2. Ethylene Polymerization Activities of $Ti(OR)_4$ - $MgCl_2$ Milled Catalysts

No.	Milling conditions				Ti contents mg/g	Activities ⁵⁾ g-PE/mM-Ti
	Methods	$Ti(OR)_4$	Ti/Mg M/M	Times hr		
1 ¹⁾	R ³⁾	$Ti(OBu)_4$	0.05	25	20	9640
2	V ⁴⁾	"	0.077	20	26	9260
3 ²⁾	"	"	0.10	"	30	6860
4 ²⁾	R	$Ti(OEt)_4$	0.05	64	23	7140

1) MFR = 2.6 g/10' 2) MFR = 6.5 g/10'

3) Rotatory mill method 4) Vibratory mill method

5) Pressurized polymn.

References

- 1) Montecatini Edison Co., Br. Pat. 1286867 (1968)
Mitsui Petrochemicals Industries, LTD., Italy Pat. 912345 (1968)
- 2) N. Kashiwa, Polymer J. 12, 603 (1980)
- 3) P. Galli et al., Eur. Polym. J. 19, 19 (1983)

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