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A highly non-stereospecific catalyst for propene polymerization

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SUMMARY

The $MgCl_2$-supported $TiCl_3$ catalyst containing a small amount of Ti(about 0.1 wt.%) was prepared by treating the mixture of $MgCl_2$ and $TiCl_3$ 3py with an excess amount of $AlEt_2Cl$. Propene polymerization was conducted at 40°C by using $AlEt_3$ as cocatalyst. The catalyst system was found to be highly active, which gave atactic polypropylene

INTRODUCTION

Enormous efforts have been made to develop highly active and highly isotactic-specific catalysts for propene polymerization, which have brought about the highly efficient industrial process to produce isotactic polypropylene. On the other hand, the use of atactic polypropylene has been recently increased. It is well known that homogeneous catalyst systems composed of some transition metal compounds and methylalumoxane, which were developed by Kaminsky and Sinn, effectively produce atactic polypropylene (1). However, the structure of this polymer(random) is quite different from that of atactic polypropylene produced by heterogeneous catalysts. Atactic polypropylene produced by heterogeneous catalysts is composed of isotactic and syndiotactic stereoblocks(2), therefore, it is more useful as elastomers, etc.(3). Thus, it seems to be of great interest to develop highly active heterogeneous catalysts which selectively produce atactic polypropylene. Usual $MgCl_2$-supported Ti-based catalysts produce polypropylene containing more than 20 wt.% of isotactic parts even in the absence of any Lewis bases(internal and external donors). The authors previously investigated the effects of internal and external donors on propene polymerization with $MgCl_2$-supported $TiCl_4$ catalysts in detail and proposed the mechanism that the isolated donor-free Ti^{3+} species having two chlorine vacancies give atactic polypropylene while bi- or multinuclear Ti^{3+} species give isotactic one(4). Based on this mechanism, it may be expected that the highly dispersed Ti-based catalysts selectively produce atactic polypropylene. From such a viewpoint, a non-stereospecific catalyst for propene polymerization was explored by decreasing the Ti content in $MgCl_2$-supported catalysts.

RESULTS AND DISCUSSION

In Fig. 1 are shown typical kinetic curves of the propene polymerization obtained with the present catalyst as well as a usual supported catalyst($TiCl_4/MgCl_2$; Ti content 2.8 wt.%). The present catalyst showed a very high initial activity, but it drastically decreased within first ten minutes. The average activity for 2 h was about 6 kg-PP/g-Ti·h.

As shown in Tab. 1, a usual $MgCl_2$-supported catalyst even in the absence of internal and external donors gave polypropylene having 27wt.% of

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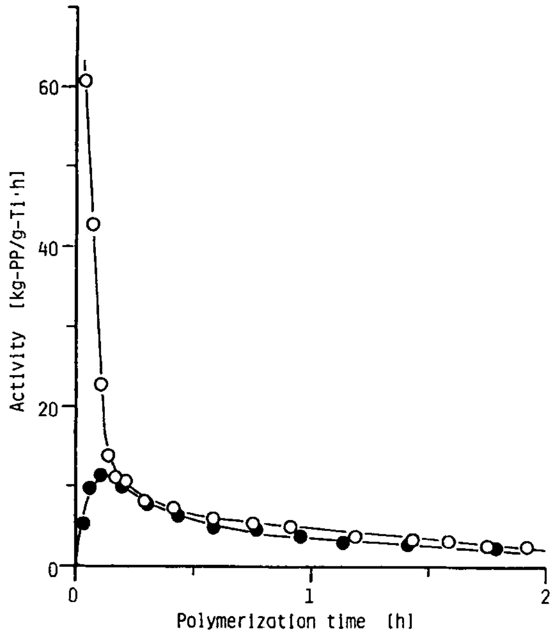


Figure 1 Kinetic curves of propene polymerization
○ ;$TiCl_3/MgCl_2$-$AlEt_3$
● ;$TiCl_4/MgCl_2$-$AlEt_3$

isotactic fraction(Run No. 3). On the contrary, the present catalyst system showed very low isotactic-specificity(Run No. 1). The isotactic triad fractions(mm) of heptane soluble parts of samples 1 and 2 were 0.54 and 0.39, suggesting that these polymers are not random but stereoblock as described above. The number average molecular weight of these atactic polymers were $1.3x10^4$ and $2.5x10^4$, respectively.

These results may be interpreted as follows. The present catalyst was prepared from $TiCl_3$·3py in which the $TiCl_3$ crystal should be perfectly destroyed. By treating the mixture of $MgCl_2$ and $TiCl_3$· 3py with a Lewis acid like $AlEt_2Cl$, the pyridine coordinated with $TiCl_3$ is removed to result in forming mononuclear $TiCl_3$ species on the $MgCl_2$ suface (Scheme 1). Since polymerization took place even in the absence of $AlEt_3$(Run No. 2), Ti species might be partly alkylated by $AlEt_2Cl$ in this process(Step I). However, the addition of $AlEt_3$(Step II) is neccessary to activate the catalyst. It has been already proposed that such mononucler Ti^{3+} species having two chlorine vacancies selectively give atactic polymer(4,5).

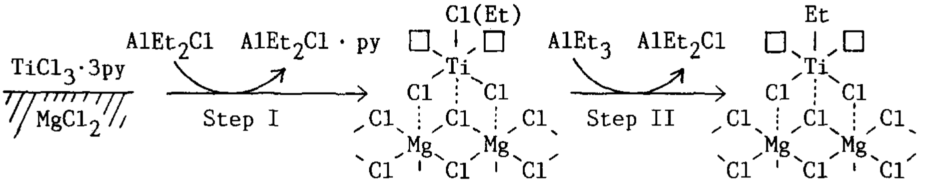
In the case of $TiCl_4$-based catalysts, on the other hand, $TiCl_4$ is instantaneously reduced by $AlEt_3$ and the resulting $TiCl_3$ may form cluster-like particles, which may give rise to isotactic-specific Ti species. Even in the present $TiCl_3$-based system, such isotactic-specific Ti species were found to be formed when the content of Ti was increased(6).

In summary, we could prepare a highly non-stereospecific catalyst for propene polymerization by supporting less content of $TiCl_3$ on $MgCl_2$. A more

Table 1 Results of propene polymerization.

Run No.	Ti-supported	Polymerization conditions			Activity	I.I.[a]
		pressure	TEA	Time		
	[wt.%]	[bar]	[mmol·dm^{-3}]	[h]	[kg-PP/g-Ti·h]	[%]
1	0.12	1	10	2	6.0	6
2[b]	0.09	c.a.20	0	2	0.6	12
3	2.8	1	10	2	4.5	27

a) Weight fraction of boiling heptane insoluble, isotactic polymer.
b) Polymerization was conducted by 100 ml stainless steel autoclave containing 9 l(S.T.P.) of propene.



Scheme 1

A plausible scheme for the formation of non-stereospecific species.

detailed study is now being carried out and the results will be reported in another paper.

EXPERIMENTAL

Materials: Propene (from Mitsubishi Petrochemical Co.), MgCl$_2$ and titanium-reduced TiCl$_3$ (from Toho Titanium Co.) were used without further purification. Research grade heptane commercially obtained was purified according to the usual procedures. Nitrogen of 99.9995 % purity (from Nihon Sanso Co.) was used after passing through the 3A molecular sieve column. Other chemicals (research grade) were commercially obtained and used without further purification.

Preparation of the MgCl$_2$-supported TiCl$_3$ catalyst: TiCl$_3$·3Py was prepared from the reaction of TiCl$_3$ with pyridine at room temperature. The mixture of MgCl$_2$ and TiCl$_3$·3py was treated with an excess amount of AlEt$_2$Cl in heptane under vigorous stirring, followed by washing with plenty of heptane to obtain the catalyst. It was confirmed from the elemental analysis that pyridine was completely removed by this process.

Polymerization and analytical procedures: Polymerization of propene was usually carried out in a 0.3 dm^3 glass reactor equipped with a magnetic stirrer. Measured amounts of the catalyst and AlEt$_3$ (TEA) were added to the reactor containing 0.1 dm^3 of heptane. Propene was continuously introduced to keep the total pressure at 1 bar. Polymerizaiton was terminated by adding a dilute hydrochloric acid solution in methanol. The polymer was fractionated by extracting with boiling heptane. Molecular mass distribution (MMD) of the polymer was determined at 140°C by GPC (Shodex LC HT3) using o-dichlorobenzene as solvent. The contents of titanium in the catalysts were determined by atomic absorption spectrophotometry (Shimadzu AA-6105). The ^{13}C NMR spectrum of the polymer was recorded at 120°C using a JEOL FX-100 spectrometer in the pulse Fourier-Transform(FT) mode. Sample solutions were made in 1,2,4-trichlorobenzene/benzene-d$_6$ (9/1 in vol.) up to 12 wt.%.

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