

고활성촉매를 사용한 프로필렌 중합 : I. 촉매의 제조

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Polymerization of Propylene with High-Activity Catalysts I. Preparation of Precatalysts

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INTRODUCTION

The high-activity supported catalysts based on $TiCl_4$ for propylene polymerization have been developed by many companies.¹ These solid precatalysts are prepared from $MgCl_2$, $TiCl_4$ with or without Lewis base(LB), and used for polymerization of propylene in conjunction with AlR_3 as a cocatalyst. The various routes are announced to prepare the high-activity supported catalysts^{2,3} and the techniques employed for the treatment of $MgCl_2$ supporter are ball-milling, vibration milling, spraying and precipitation for physical methods as well as the enormous variety of chemical conversions starting from almost every conceivable magnesium salt. However, there is few scientific reports but patents⁴ on the precipitation treatment of $MgCl_2$ for the propylene polymerization with supported catalyst systems.

In this report the effects of $MgCl_2$ precipitation temperature and concentration of LB as a component of the precatalyst (internal LB) and/or cocatalyst (external LB) on the yield and isotactic index(I.I.) have been studied.

EXPERIMENTAL

Preparation of Precatalysts

A three-necked flask, fully purged with dry

N_2 , was charged with xylene, commercially available $MgCl_2$ (Toho Titanium Co., Japan) and anhydrous EtOH with or without ethylbenzoate(EB) as internal LB. The mixture was heated with stirring at 125°C for 20 minutes and poured into the flask containing cold hexane (dried over molecular sieve) with stirring. The resulting $MgCl_2$ solid was collected by decantation and washed thoroughly with hexane. $TiCl_4$ in excess quantity and the treated $MgCl_2$ suspended in hexane were reacted with stirring at 100°C for 2 hours. The obtained precatalyst was washed thoroughly with plenty of hexane. The Ti content of the precatalyst was determined by UV-visible spectrophotometer (Varian Cary 219 spectrotometer) using absorbance at 392 nm.⁵

Polymerization

The propylene polymerization was carried out in a stainless steel autoclave (Parr, U.S.A.) at 50°C. Appropriate amounts of hexane, $Al(C_2H_5)_3$, EB as external LB when required, and the precatalyst were added in this order. After 10 minutes of aging time, the propylene was fed continually to maintain a constant total pressure of 4 kg/cm². The polymerization was stopped after one hour using small amount of methanol, and the polypropylene(PP) was co-

agulated by pouring into plenty of methanol, filtered and dried under vacuum. The yield (kg-PP/g-Ti·h·atm) was calculated from the weight of PP obtained and the I. I. was determined as the weight fraction of PP remaining insoluble after the extraction with boiling heptane.

Table 1. Preparation Condition of Precatalysts

Precatalyst system	Precipitation temp.(°C)	Internal LB	Ti content (wt%)
A ₁	20		9.8
A ₂	0	none	12.0
A ₃	-23		8.6
B ₁	20		11.5
B ₂	0	EB	10.4
B ₃	-23		9.4
Milling		none	5.4

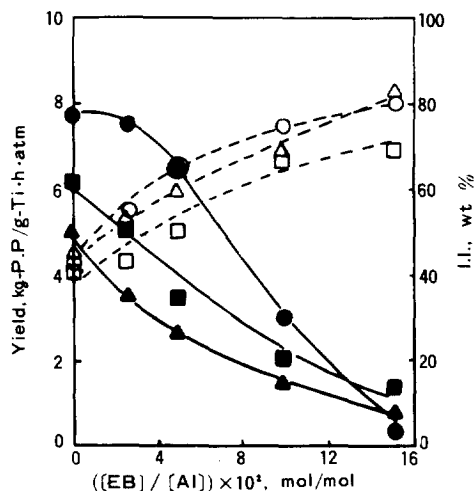


Fig. 1. Effect of $[EB]/[Al]$ on the yields (●▲■) and I. I. (○△□) of polymers produced with catalyst A₁ (●○), catalyst A₂ (▲△) and catalyst A₃ (■□)

$$A_1 : [Ti] = 1.40 \times 10^{-4} \text{ mol/l}$$

$$A_2 : [Ti] = 1.40 \times 10^{-4} \text{ mol/l}$$

$$A_3 : [Ti] = 1.20 \times 10^{-4} \text{ mol/l}$$

$$\frac{[Al]}{[Ti]} = 40, T = 50^\circ\text{C}$$

$$t_a = 10 \text{ min}, t_p = 60 \text{ min.}$$

T: polymerization temperature,

t_a: aging time, t_p: polymerization time.

RESULTS AND DISCUSSION

The values of Ti content of precatalysts obtained at various conditions are shown in Table 1. The Ti contents were found to be 9-12wt% which were found to be almost independent of MgCl₂ precipitation temperature and presence/or absence of EB as internal LB. This value of Ti content was higher than that obtained using MgCl₂ milling method⁶ but similar to that of the MgH₂-supported precatalyst.⁷

In the case of MgCl₂-supported Ziegler-Natta catalysts, the effects of LB such as EB are so remarkable that the addition of such compound seems to be inevitable in practice.⁸ Therefore, the concentration effects of internal LB as a component of precatalyst and external LB as a component of cocatalyst were investigated.

The change of the yield and I. I. with con-

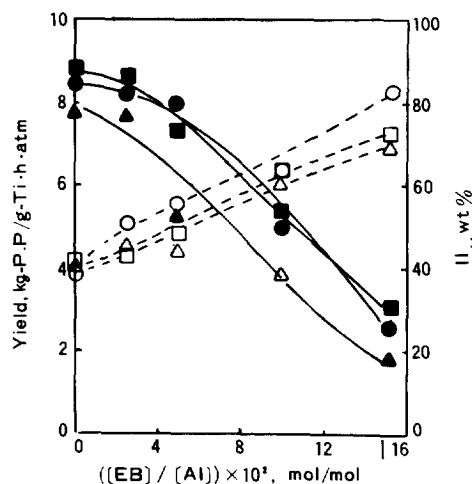


Fig. 2. Effect of $[EB]/[Al]$ on the yields (●▲■) and I. I. (○△□) of polymers produced with catalyst B₁ (●○), catalyst B₂ (▲△) and catalyst B₃ (■□)

$$B_1 : [Ti] = 1.20 \times 10^{-4} \text{ mol/l}$$

$$B_2 : [Ti] = 1.40 \times 10^{-4} \text{ mol/l}$$

$$B_3 : [Ti] = 1.40 \times 10^{-4} \text{ mol/l}$$

$$\frac{[Al]}{[Ti]} = 40, T = 50^\circ\text{C}$$

$$t_a = 10 \text{ min}, t_p = 60 \text{ min.}$$

centrations of EB as external LB but in the absence of internal LB was shown in Fig. 1 for various precatalysts. From this figure it was found that the changes of $MgCl_2$ precipitation temperature showed some variation of yield but gave few effects on I.I.. In addition, the increase in EB concentration resulted in lower yield but higher I.I. due to decrease in formation of heptane-soluble PP.⁹

In the presence of internal LB, the yield and I.I. were plotted against concentration of EB as external LB in Fig. 2. It could be seen that the changes of yield and I.I. with concentration of EB have similar tendency to those without internal LB.

By comparing Fig. 1. and Fig. 2, it was found that the presence of internal LB resulted in more yield and gave less effect of $MgCl_2$ precipitation temperature on yield than the absence of internal LB did. So it can be concluded to be desirable that the internal LB be added for the precipitation method of $MgCl_2$ treatment.

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