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Effect of Ethanol Treatment in the Preparation of $MgCl_2$ Support for the Propylene Polymerization Catalyst

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Introduction

Highly active Ziegler−Natta catalysts for propylene polymerization prepared by impregnating $TiCl_4$ on $MgCl_2$ have been reported in the literature.[1−3] In order to overcome the low surface area of $MgCl_2$ and its poor interaction with $TiCl_4$, many studies on the treating methods of $MgCl_2$ have been carried out.[4−5] The most widespread preparation method of active $MgCl_2$ is ball-milling of anhydrous $MgCl_2$ together with $TiCl_4$ or treatment of the $MgCl_2$−electron donor complexes obtained by ball-milling with $TiCl_4$.[7] The main advantage of ball-milling lies in obtaining small crystallites of $MgCl_2$ in order to introduce a sufficient amount of titanium species into the crystal lattice of $MgCl_2$.[8] However, the ball-milling method has a disadvantage: Control of polymer morphology is difficult because the morphology of the polymer has a tendency to duplicate that of the catalyst. Therefore, many other methods for the catalyst preparation, such as recrystallization[9] and chemical conversion[10] of Mg compounds, have also been studied in order to overcome the disadvantage of the ball-milling method.

In this work, Ziegler−Natta catalysts were prepared by the recrystallization method reported in our previous work[11] using different amounts of ethanol. Ethanol was used as a solvent for $MgCl_2$. Di-*n*-butyl phthalate (DNBP) as an internal electron donor was introduced into the ethanol solution of $MgCl_2$. This solution was mixed with *n*-decane to prevent recrystallized $MgCl_2$ from aggregating. The ethanol solution was emulsified in an *n*-decane medium by vigorous stirring of the mixture and was in situ dried in vacuum. Due to the difference in boiling points between *n*-decane and ethanol, only ethanol was eliminated during vacuum drying and the crystallized $MgCl_2$ particles did not aggregate. After the prepared $MgCl_2$ was treated with triethylaluminium (TEA), $TiCl_4$ was impregnated on the modified $MgCl_2$ support.

Propylene was polymerized with the catalyst and TEA as a cocatalyst in the presence or absence of ethyl benzoate (EB), and external electron donor. In this study, the effect of the ethanol treatment in the preparation of $MgCl_2$ by the recrystallization method on the catalyst activity and the isotactic index (II) of polypropylene was examined.

Experimental Section

Catalyst Preparation. Anhydrous $MgCl_2$ (0.05 mol, 4.76 g) was introduced into a glass reactor equipped with a magnetic stirrer, and then 30 mL of ethanol (EtOH) was added to the reactor under a stream of dry N_2. The mixture was heated to 60 °C and stirred until $MgCl_2$ was completely dissolved. Then 0.005 mol (1.334 mL) of DNBP was introduced into the solution, and the mixture was refluxed for 2 h. *n*-Decane (100 mL) was added to the solution, and the mixture was stirred vigorously for 1 h and dried under vacuum at 70 °C. $MgCl_2$ particles were slowly precipitated in the *n*-decane medium as EtOH evaporated. The resulting $MgCl_2$ particles were washed four times with *n*-heptane to remove *n*-decane and residual EtOH and then dried under vacuum to remove the *n*-heptane (MDE30-S). MDE30-S (5 g) was introduced into a 500 mL flask equipped with a water condenser and a magnetic stirrer. TEA (1 M) (150 mL) was added to the flask followed by 100 mL of *n*-heptane. The mixture was heated at 80 °C and left for 2 h for the reaction to occur. Then the mixture was washed five times with *n*-heptane to remove unreacted TEA and finally dried under vacuum (MDE30-T). $TiCl_4$ (30 mL) was introduced into MDE30-T, and the mixture was heated at 80 °C and left for 2 h for the reaction to occur. After that, the mixture was washed six times with *n*-heptane and suspended in 150 mL of *n*-heptane (MDE30-C). MDE100-C was also prepared by using 100 mL of EtOH. The preparation method of MDE100-C was the same as that for MDE30-C.

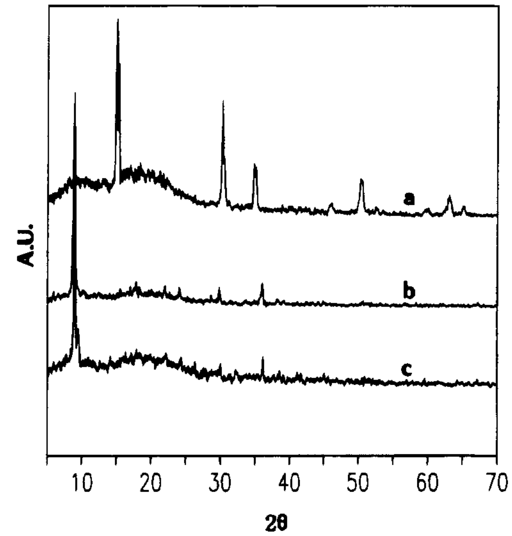

Figure 1. XRD pattern of (a) $MgCl_2$, (b) MDE30-S, and (c) MDE100-S.

Polymerization. A 500 mL glass reactor equipped with a magnetic stirrer was used for polymerization. The reactor was purged with N_2 and evacuated three times. *n*-Heptane (150 mL) was introduced into the reactor followed by TEA which was used as a cocatalyst in the presence or absence of EB. The reactor was immersed in a bath at 50 °C, and propylene was charged into the reactor at 1.3 atm until the solvent was saturated with propylene. Finally, the catalyst suspension was introduced into the reactor with a syringe. Catalytic activity was determined from the amount of consumed propylene measured by a mass flow meter.

Results and Discussion

Anhydrous $MgCl_2$ has the cubic close packing structure giving strong a XRD pattern at $2\theta = 35°$ (004 plane), 15° (003 plane) and 50° (110 plane).[9] However, the XRD pattern varies depending on the amount of alcohol in $MgCl_2$. We found that characteristic XRD patterns of MDE30-S and MDE100-S developed at higher 2θ and the peak intensities were weaker compared with those of $MgCl_2$ as shown in Figure 1. This means that $MgCl_2 \cdot n$EtOH was formed when $MgCl_2$ was prepared by the recrystallization method. When these supports were treated with TEA, they changed into an amorphous state due to the removal of EtOH in the form of aluminum ethoxide which was formed by reaction of TEA with EtOH in $MgCl_2 \cdot n$EtOH, as reported in our

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Table 1. Characterization of Supports and Catalysts

	surface area (m^2/g)	EtOH content (wt %)	DNBP content (wt %)	avg particle size (μm)	Ti content (wt %)
MDE30-S[a]	8.1	62.3	6.84	35.6	
MDE30-T[b]	101.5	19.7	0.91	17.6	
MDE30-C[c]	112.6	5.57	0.39	14.1	5.71
MDE100-S[d]	12.1			25.2	
MDE100-C[e]	180.6			13.8	3.99

[a] $MgCl_2$/DNBP/EtOH (30 mL). [b] $MgCl_2$/DNBP/EtOH (30 mL)/TEA. [c] $MgCl_2$/DNBP/EtOH (30 mL)/TEA/$TiCl_4$. [d] $MgCl_2$/DNBP/EtOH (100 mL). [e] $MgCl_2$/DNBP/EtOH (100 mL)/TEA/$TiCl_4$.

previous work.[11] This result was also confirmed by the fact that the surface area of MDE30-S drastically increased and the EtOH content decreased after the treatment with TEA, as shown in Table 1. Considering the fact that the amount of EtOH in MDE30-T further decreased after the Ti impregnation, it is likely that EtOH was also removed in the form of titanium ethoxide by the reaction of EtOH with $TiCl_4$. Although all organic compounds in the support were not removed after the treatment with TEA and $TiCl_4$, it was found that the surface heterogeneity of the supports and catalysts increased when EtOH was removed in the form of aluminum ethoxide and titanium ethoxide.

Table 1 also shows the properties of the prepared catalysts. MDE100-S has a larger surface area and a smaller particle size than MDE30-S. This means that the $MgCl_2$ support with a smaller particle size was formed during recrystallization when it was treated with very large amounts of EtOH due to the decreased $MgCl_2$ concentration in EtOH droplets in the *n*-decane medium. In addition, it is likely that EtOH in MDE100-S with a smaller particle size has a much higher probability of reacting with TEA than in MDE30-S. This means that MDE100-S rather than MDE30-S undergoes an enhanced EtOH removal upon treating with TEA. On the other hand, EtOH in MDE30-T rather than in MDE100-T has a much higher probability of reacting with $TiCl_4$. Considering the result that the Ti content in MDE100-C is lower than in MDE30-C, it can be inferred that the large amounts of aluminum ethoxide in MDE100-T compared to that in MDE30-T retard the Ti impregnation on the support and the remaining EtOH in MDE30-T rather than in MDE100-T reacts more with Ti to form inactive titanium ethoxide.

Figure 2 shows the catalytic activity and II values as a function of the EB/Al mole ratio. MDE100-C shows a higher activity and a higher II than MDE30-C in the presence of EB. MDE100-C also showed a higher catalytic activity and a higher II than MDE30-C in the absence of EB. We believe that the enhanced II of MDE100-C is mainly due to very large amounts of aluminum ethoxide acting as an electron donor, as in the case of our previous work.[11] The enhanced activity of MDE100-C is due to the following two factors: (1) large amounts of aluminum ethoxide in MDE100-T retarding the Ti impregnation on MDE100-T, and (2) small amounts of EtOH in MDE100-T forming small amounts of inactive titanium ethoxide upon Ti impregnation.

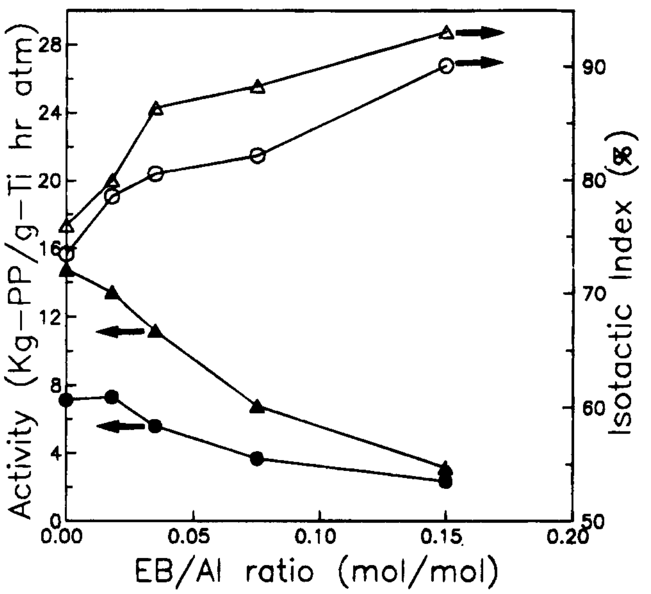

Figure 2. Catalytic activity and isotactic index as a function of the EB/Al mole ratio at 50 °C and 1.3 atm when Al/Ti = 70:MDE100-C (△, ▲), MDE30-C (○, ●).

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