Study on Propene Polymerization Using a Novel Spherical Ziegler-Natta Catalyst and Its Kinetics

Zhao-yang Ye, Li Wang, Shan Jiang

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

ABSTRACT: The effects of the Al/Ti ratio and external donor (ED) on the catalytic activity and kinetics of propene polymerization catalyzed by a spherical Ziegler-Natta (Z-N) catalyst were investigated. The preparation conditions of the catalyst play an important role in the polymerization kinetics. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3737–3740, 2003

Key words: kinetics (polym.); catalysis;

INTRODUCTION

Heterogeneous Ziegler-Natta (Z-N) catalysts with $MgCl_2$ as a support have a greatly improved activity and stereospecificity.[1–3] Recently, catalysts supported on spherical $MgCl_2$ adducts afforded spectacular progress in controlling polymer morphology as spherical particles,[4–8] by making use of the replication phenomenon reported many years ago.[2] However, the kinetics study of the spherical Z-N catalysts has not been done extensively.

In our previous article,[9–11] we introduced a novel method of preparing spherical $MgCl_2$ supports, and investigated different factors that influence the morphology and size of the supports. In this article, kinetics of the polymerization reactions with a spherical catalyst was investigated. The influence of the Al/Ti ratio and external donor (ED) on the catalytic activity and kinetics of propene polymerization are evaluated, and possible reaction mechanisms are proposed.

EXPERIMENTAL

Materials

Spherical catalysts with $TiCl_4$ supported on $MgCl_2$ have been prepared earlier.[11] $AlEt_3$ (Fluka) and di-i-butylphthalate (DIBP) (Acros) were used as received. Diphenyldimethoxysiane (DPDMS), ethanol, paraffin oil, and methyl siloxane were dried over 4-Å molecular sieves before use. Toluene, petroleum ether, and heptane were purified by refluxing over an Na-K alloy under nitrogen and dried over 4-Å molecular sieves prior to use. Polymerization-grade propene was further purified by passing over 4-Å molecular sieves. All manipulations of air- and/or moisture-sensitive materials were carried out in an inert atmosphere using a dual vacuum/argon line and a standard Schlenk technique.

Polymerizations

Polymerization reactions at 1 atm were performed in a 150-mL, three-necked glass reactor. Required amounts of petroleum ether, $AlEt_3$, DPDMS, and the catalyst were added into the reactor. The propene pressure was kept constant by continuous feeding of propene. The reactions were terminated by the addition of ethanol, which contained 5 wt % HCl. The polymer was filtered off, washed with methanol, and dried.

RESULTS AND DISCUSSION

The effect of Al/Ti ratio on the catalytic activity

Table I shows different preparation conditions and the Ti contents in the resultant catalysts.

It is supposed that the cocatalyst $AlET_3$ has two main roles: one is to remove impurities in the polymerization, and the other is to react with the catalyst to generate active species. Tables II and III, and Figures 1 and 2 show the relationship between catalytic activity and the Al/Ti ratio. Two types of dependencies between catalyst activity and the Al/Ti molar ratio were observed. Catalysts 10315c1 and 10418c3 belong to the same type, while catalysts 10418c1 and 10418c2 belong to another type. This indicates that the reaction between the $AlET_3$, ED and the supported catalyst is quite complex.

For catalysts 10315c1 and 10418c3, when the amount of the $AlET_3$ is small, the catalytic activity is very low. Most of the $AlET_3$ in such runs is used to remove

TABLE I
Treatment Temperatures and Ti Content in the Catalysts

Catalyst	Temperature (°C)[a]	Temperature (°C)[b]	Ti Loaded (wt %)
10315c1	130	130	2.66
10317c1	130	130	1.50
10316c1	130	130	2.60
10316c2	80	130	4.65
10418c1	90	90	5.99
10418c2	110	110	6.21
10418c3	130	130	5.06

[a] The $TiCl_4$ treatment is carried out twice; this is the temperature for the first time.
[b] The treatment temperature for the second time.

impurities, and only a little is left to activate the catalytic center. The catalytic activity increases as the amount of the $AlET_3$ increases until an optimum Al/Ti ratio is reached. The decrease of the catalytic activity with the further increase of $AlET_3$ amount may be due to reduction of Ti to a low valence.

The effect of Al/Ti ratio on the kinetics

Figures 3 and 4 show two typical kinetic profiles for the polymerization catalyzed by spherical Z-N catalyst. Catalyst 10316c1 was treated with $TiCl_4$ at a

TABLE II
Catalytic Activity with Different Al/Ti

Al/Ti (mol/mol)	Activity [kgPP/(gTih)]		
	10418c3[a]	10418c1[b]	10418c2[b]
50	0.75	0.96	1.10
80	1.97	0.75	0.59
100	2.00	1.05	1.01
150	1.07	0.45	1.38

[a] $T = 55°C$, $P = 1$ atm, $t = 30$ min, 50 mL toluene, cocatalyst: $AIET_3$, ED: DPDMS, ED/Ti (mol/mol) = 2.0;
[b] $T = 60°C$, $P = 1$ atm, $t = 30$ min, 50 mL toluene, cocatalyst: $AIET_3$, ED: DPDMS, ED/Ti (mol/mol) = 2.0;
T is temperature, P is pressure, t is reaction duration, ED is external donor.

TABLE III
Propylene Polymerization Results with Different ED/Ti Using Catalyst 10317c1[a]

ED/Ti (mol/mol)	Activity [kgPP/(gTih)]
0	1.28
1.3	0.5
2.7	0.64
5.3	0.79
8.0	3.38
13.3	0.99
26.7	0.41

[a] $T = 60°C$, $P = 1$ atm, $t = 30$ min, 50 mL toluene, cocatalyst: $AIET_3$, ED: DPDMS, Al/Ti (mol/mol) = 133.3.

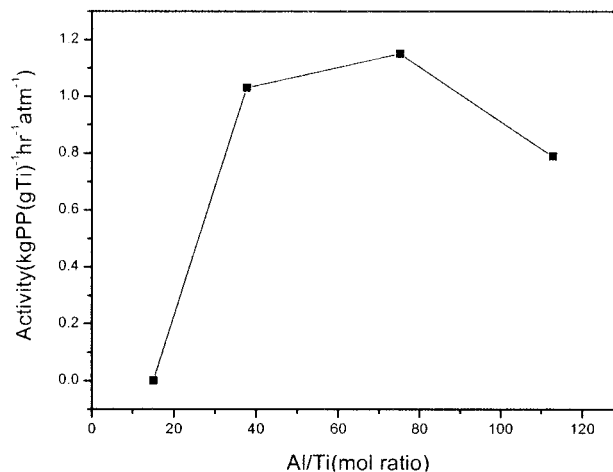**Figure 1** Catalytic activity at different Al/Ti using catalyst 10315c1. $T = 60°C$, $P = 1$ atm, $t = 30$ min, 50 mL, hexane, cocatalyst; $AIET_3$, ED: DPDMS, ED/Al (mol/mol) = 0.04.

higher temperature. This affects some properties, for example, morphology of the prepared catalyst and, therefore, changes the polymerization behavior. The 10316c1 catalyst has a much looser morphology due to the higher synthesis temperature, so that the cocatalyst is able to reactivate the entire Ti centers immediately. On the other hand, the cocatalyst can only reactivate catalyst 10418c2 step by step because of the compact morphology of catalyst. In this way, the kinetics of 10316c1 shows a rapid decay after initiation, whereas 10418c2 shows a smoother profile.

The influence of ED/Ti on the catalytic activity

It is generally known that adding the ED will enhances the stereospecificity but decreases the overall
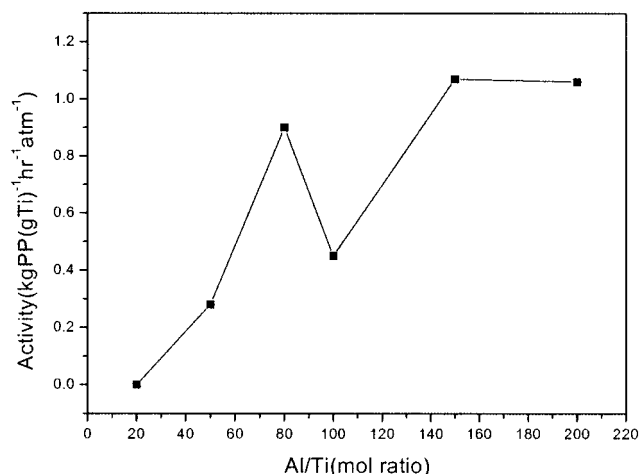

Figure 2 The influence of Al/Ti on propylene polymerization activity using catalyst 103156c2; $T = 60°C$, $P = 1$ atm, $t = 30$ min, 50 mL, toluene, cocatalyst; $AIET_3$, ED: DPDMS, ED/Al (mol/mol) = 0.04.
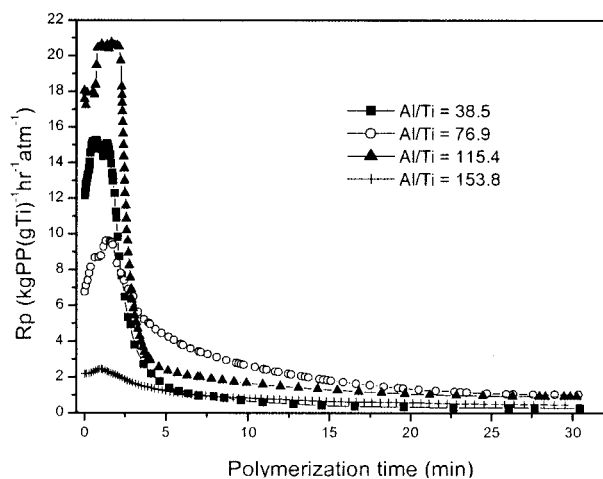
Figure 3 Propylene polymerization results at different Al/Ti using catalyst 10316c1; $T = 60°C$, $P = 1$ atm, $t = 30$ min, 50 mL, toluene, cocatalyst; $AlET_3$, ED: DPDMS, ED/Al (mol/mol) = 0.04.

catalytic activity. A possible explanation is that ED converts the atactic species to the isotactic ones and stabilizes the isotactic active centers, but too much ED may deactivate the active centers. It is important to adjust the amount of the ED to an optimum. Our results, Tables III and IV, show that the highest activity for catalyst 10317c1 reaches at ED/Ti = 8.0, as well as Ed/Ti = 2.0 for catalysts 10418c2 and 10418c3.

The influence of ED/Ti on the kinetics

Figure 5 shows that adding of the external donor changes the kinetic behavior of the polymerization. When ED/Ti = 0, $AlET_3$ can activate most of the active
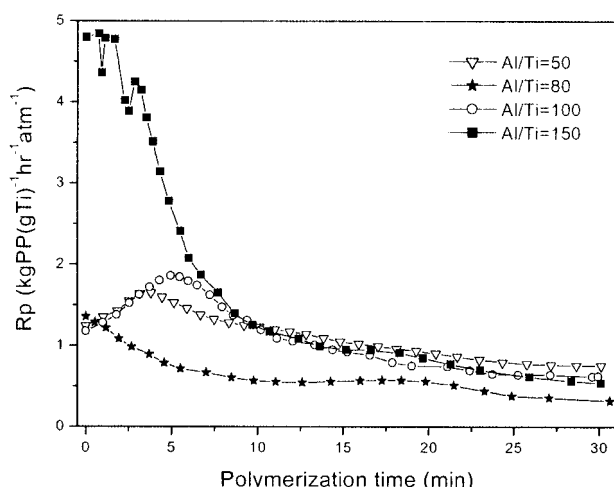

Figure 4 The influence of Al/Ti on propylene polymerization kinetics using catalyst 10418c2; $T = 60°C$, $P = 1$ atm, $t = 30$ min, 50 mL, toluene, cocatalyst; $AlET_3$, ED: DPDMS, ED/Ti (mol/mol) = 2.0.

TABLE IV
Propylene Polymerization Results with Different ED/Ti Using 10418c2 and 10418c3

ED/Ti (mol/mol)	Activity (kgPP/(gTih))	
	10418c2[a]	10418c3[b]
0	0.47	0.87
1.0	0.91	1.74
2.0	1.09	2.39
4.0	0.93	1.66
6.0	0.74	0.62
10.0	0.57	0.49

[a] $T = 67°C$, $P = 1$ atm, $t = 30$ min, 50 mL toluene, cocatalyst: $AlET_3$, ED: DPDMS, Al/Ti (mol/mol) = 50.0.
[b] $T = 70°C$, $P = 1$ atm, $t = 30$ min, 50 mL toluene, cocatalyst: $AlET_3$, ED: DPDMS, Al/Ti (mol/mol) = 50.0.
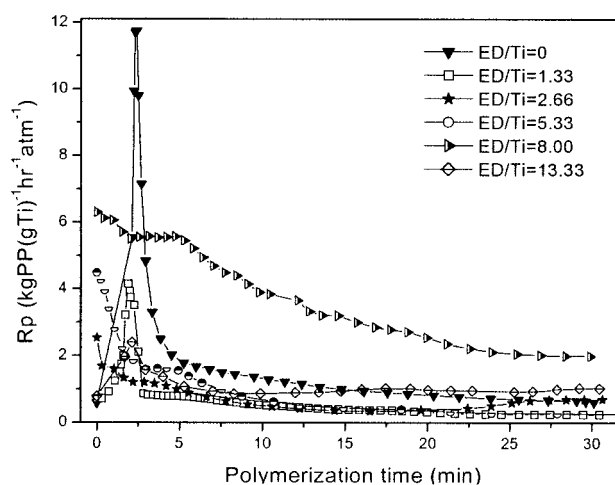

Figure 5 The influence of ED/Ti on propylene polymerization kinetics using catalyst 10317c1; polymerization conditions are the same as Table III.
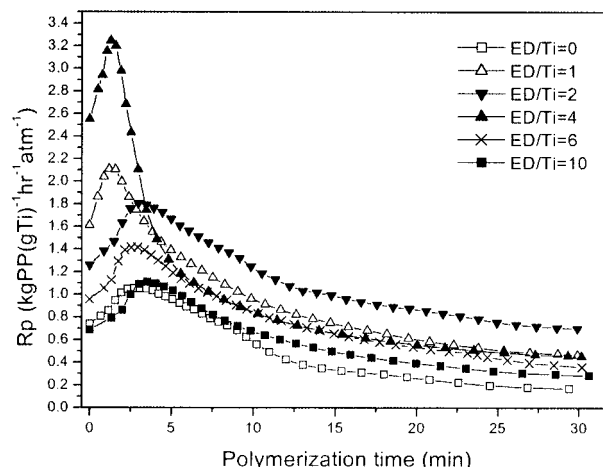

Figure 6 The influence of ED/Ti on propylene polymerization kinetics using catalyst 10418c2; polymerization conditions are the same as Table IV.

center rapidly, then follows a fast decay. After adding the ED, the kinetic profile becomes smoother. Samson et al.[12] supposed that ED may form a complex with $AlET_3$ and release $AlET_3$ gradually, which reduces activity of $AlET_3$. In this way, the formation of the active centers is slowed down.

Figure 6 shows that the effect of adding of ED on the kinetic behavior of 10418c2 is different from that of 10317c1. This may be due to the different morphology of the catalysts obtained under different preparation conditions.

CONCLUSIONS

The preparation conditions of the spherical Z-N catalyst play an important role in the polymerization kinetics, and they may affect the morphology of the catalyst, which will greatly change the kinetic behavior. It is important to find out the optimum Ai/Ti and ED/Ti ratios for the highest catalytic activity.

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