

Low isotactic polypropylene synthesized with a $\text{MgCl}_2/\text{AlCl}_3$ -supported Ziegler catalyst

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Abstract

A $\text{MgCl}_2/\text{AlCl}_3$ -supported Ziegler–Natta catalyst is prepared and low isotactic polypropylene is synthesized using this catalyst in the paper. The results indicate that the polymerization activity of the $\text{MgCl}_2/\text{AlCl}_3$ -supported Ziegler–Natta catalyst is much higher than that of the MgCl_2 -supported Ziegler–Natta catalyst. And the attenuation curves of the polymerization rate of different Al/Ti molar ratios suggest the double metal active center is more stable than the single metal active center. Also the effects of the $\text{AlCl}_3/\text{MgCl}_2$ molar ratio, polymerization temperature and external electron donor on the polymerization activity and isotactic index of the products are studied in detail.

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Keywords: Ziegler–Natta catalyst; Polymerization activity; Low isotactic polypropylene

1. Introduction

Low isotactic polypropylene (LIPP), once regarded as a disposal problem in polypropylene industry, now receives more and more attention and is widely used as adhesives, sealants and coatings, additives for building top grade high way and so on [1,2]. It has been reported that the atactic polypropylene could be synthesized with some metallocene compounds [3–7], but metallocene catalytic system needs a great quantity of expensive methylaluminoxane (MAO) as cocatalyst and the existing equipment and technological process also must be changed if using these metallocene catalytic system. Therefore much effort [8–11] has been put on the development and research of economical MgCl_2 -supported Ziegler–Natta catalyst to produce LIPP.

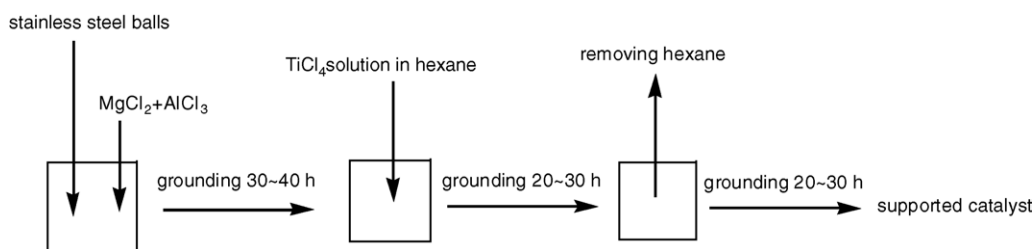
Using this heterogeneous catalysts the isolated donor-free Ti^{3+} species having two chlorine vacancies gave low isotactic polypropylene while bi- or multinuclear Ti^{3+} species gave iso-

tactic one [12]. Based on this mechanism, it may be expected that low isotactic polypropylene is mainly produced by highly dispersed Ti-based catalysts [13]. Therefore, the improvement of the polymerization activity of per-gram catalyst depends on the high specific surface area of the support.

Usually MgCl_2 is activated through being ball milled under nitrogen atmosphere in industry. After MgCl_2 being ball milled for a certain time, longer milling time leads to little further improvement in crystallite size reduction and in crystal lattice destroy and hence the polymerization activity goes to a fixed value [14]. It has been reported that AlCl_3 could promote the destroy of the crystal lattice of TiCl_3 when TiCl_3 and AlCl_3 are being co-milled [15]. Due to the similar crystal lattice structure between TiCl_3 and MgCl_2 , the crystal lattice destroy of MgCl_2 may be improved when MgCl_2 and AlCl_3 are being co-milled. Therefore, TiCl_4 can be dispersed more uniformly and fixed more firmly on the support of the $\text{MgCl}_2/\text{AlCl}_3$ -supported Ziegler–Natta catalyst than that of the MgCl_2 -supported Ziegler–Natta catalyst.

In the paper, a $\text{MgCl}_2/\text{AlCl}_3$ -supported Ziegler–Natta catalyst is prepared and low isotactic polypropylene is synthesized. The effects of the $\text{AlCl}_3/\text{MgCl}_2$ molar ratio, polymerization tem-

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Scheme 1. Preparation of the $\text{MgCl}_2\cdot\text{AlCl}_3$ -supported and low Ti-loaded catalyst with a one-pot ball milling method [16].

perature, external electron donor, the Al/Ti molar ratio on the polymerization activity and isotactic index of the products are studied in detail.

2. Experimental

2.1. Materials and the preparation of the supported catalyst

Anhydrous MgCl_2 and AlCl_3 were used as received. Hexane was refluxed over a Na–K alloy before use. AlEt_3 was obtained

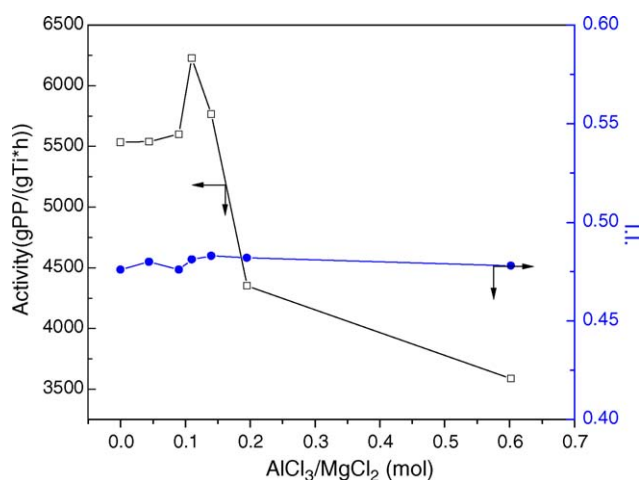


Fig. 1. Effect of the $\text{AlCl}_3/\text{MgCl}_2$ molar ratio on the propylene polymerization activity (Catalyst concentration 40 mg Cat./50 ml hexane; Ti-content of the catalyst 0.8 wt.%; the Al/Ti molar ratio 40; the polymerization temperature 40 °C; polymerization time 30 min).

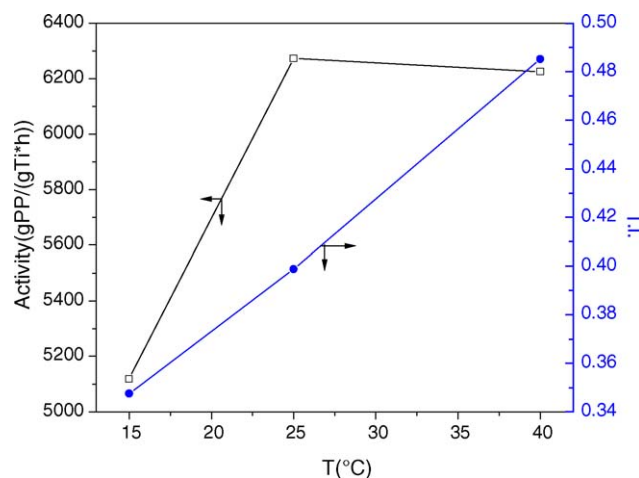


Fig. 3. Effect of the polymerization temperature on the polymerization activity and the isotactic index of polypropylene ($\text{AlCl}_3/\text{MgCl}_2$ molar ratio of the catalyst adopted 0.11; catalyst concentration 40 mg Cat./50 ml hexane; Ti-content of the catalyst 0.8 wt.%; the Al/Ti molar ratio 40; polymerization time 30 min).

commercially and used without further purification. Polymerization grade propylene was further purified by passing through two columns of pre-activated molecular sieves 4A. Nitrogen of extra pure grade, 99.99%, was dried to pass through two columns of pre-activated molecular sieves 4A to remove residual moisture and oxygen. Titanium tetrachloride and phenyltriethoxysilane were used as received.

The $\text{MgCl}_2/\text{AlCl}_3$ -supported Ziegler–Natta catalyst is prepared according to Scheme 1 [16].

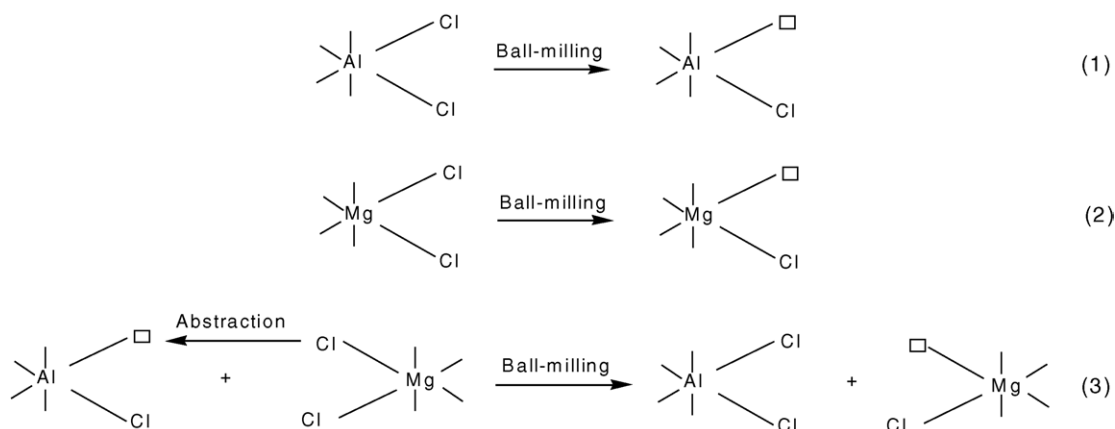


Fig. 2. The formation of defects of MgCl_2 lattice during the co-milling of MgCl_2 and AlCl_3 .

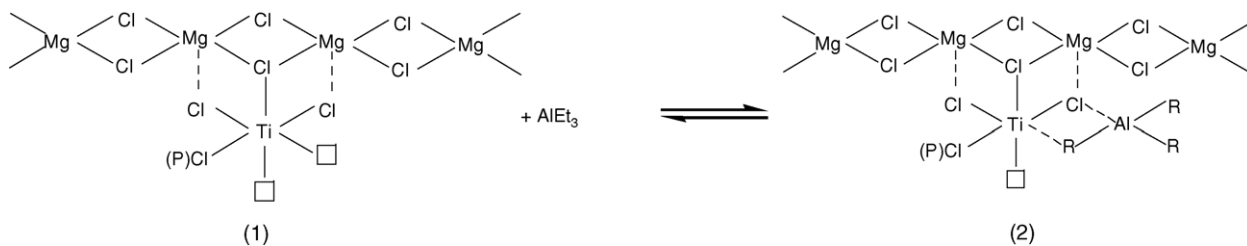


Fig. 4. The equilibrium between the single metal active center (1) and double metal active center (2) [16,17].

2.2. Propylene polymerization and the determination of the isotactic index of polypropylene

Propylene polymerization experiments were carried out in a 100 mL, three-necked glass reactor equipped with a magnetic stirrer. Required amounts of hexane, AlEt₃ and the catalyst were introduced sequentially. The pressure of propylene was kept at 1 atm. Polymerization reactions continued for 30 min and the products were precipitated by the addition of acidified alcohol. The resultant polymer was filtered off and dried in vacuum to constant weight.

The isotactic index of the resultant polypropylene was determined by the conventional solvent extraction method. The solvent used here was hexane and extraction time was 24 h. The insoluble fraction in heptane was defined as the isotactic index of the resultant polypropylene.

3. Results and discussion

3.1. Effect of the AlCl₃/MgCl₂ molar ratio on the propylene polymerization

Fig. 1 shows that the effect of the AlCl₃/MgCl₂ molar ratio on the propylene polymerization activity and isotactic index of polypropylene. The polymerization activity increases when the AlCl₃/MgCl₂ molar ratio varies from 0 to 0.11 and then

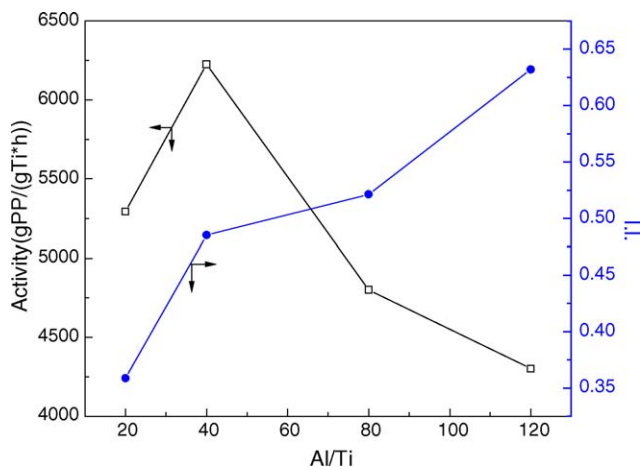


Fig. 5. Effect of the Al/Ti molar ratio on the polymerization activity and the isotactic index of polypropylene (AlCl₃/MgCl₂ molar ratio of the catalyst adopted 0.11; catalyst concentration 40 mg Cat./50 ml hexane; Ti-content of the catalyst 0.8 wt.%; the polymerization temperature 40 °C; polymerization time 30 min).

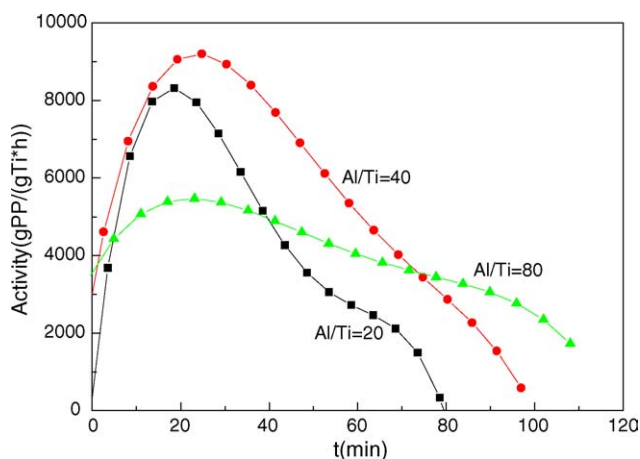


Fig. 6. The attenuation curves of the polymerization rate of different Al/Ti molar ratios (AlCl₃/MgCl₂ molar ratio of the catalyst adopted 0.11; catalyst concentration 40 mg Cat./50 ml hexane; Ti-content of the catalyst 0.8 wt.%; the polymerization temperature 40 °C).

decrease. The comparison of the polymerization activity of the MgCl₂/AlCl₃-supported Ziegler–Natta catalyst and that of the MgCl₂-supported Ziegler–Natta catalyst indicates the addition of a little amount of AlCl₃ in the process of the ball milling promotes the crystal lattice destroy of MgCl₂, which can be explained as follows. Due to the lower lattice energy of AlCl₃

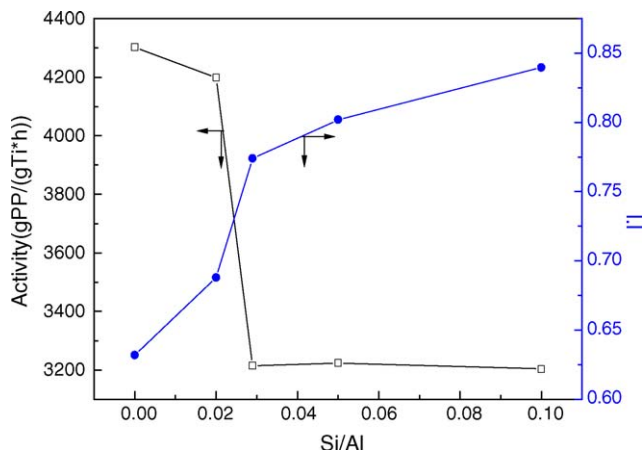


Fig. 7. Effect of the Si/Al molar ratio on the polymerization activity and the isotactic index of polypropylene (AlCl₃/MgCl₂ molar ratio of the catalyst adopted 0.11; catalyst concentration 40 mg Cat./50 ml hexane; Ti-content of the catalyst 0.8 wt.%; the Al/Ti molar ratio 120; the polymerization temperature 40 °C; polymerization time 30 min).

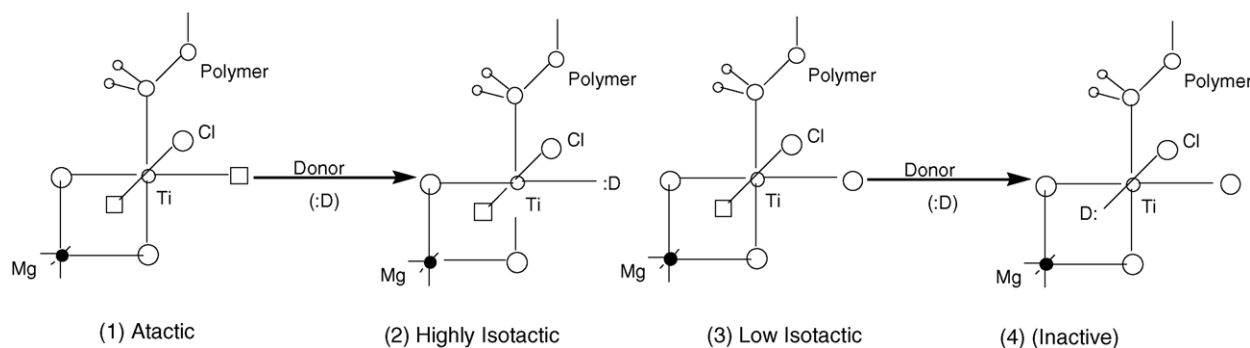


Fig. 8. Models for the active centers on supported Ti catalyst and the effect of an electron donor; (□) Cl vacancy [18].

lattice than that of MgCl_2 lattice, the lattice defects of AlCl_3 lattice is more prone to be formed than those of MgCl_2 lattice (Reaction (1) and (2), Fig. 2). The chlorine vacancies formed because of the defects of AlCl_3 lattice may attract the chlorine atoms of MgCl_2 lattice and in turn the attraction promotes the formation of the defects of MgCl_2 crystal lattice (Reaction (3), Fig. 2). Therefore, TiCl_4 can be dispersed more uniformly and fixed more firmly on the support of $\text{AlCl}_3/\text{MgCl}_2$ -supported catalyst than that of the MgCl_2 -supported catalyst.

However, the excess amount of AlCl_3 leads to the decrease of the polymerization activity. This can be explained that AlCl_3 is not an ideal support as MgCl_2 .

Also from Fig. 1, the addition of AlCl_3 of $\text{AlCl}_3/\text{MgCl}_2$ supported catalyst have little influence on the isotactic index of polypropylene in comparison with MgCl_2 supported catalyst.

3.2. Effect of the polymerization temperature on the propylene polymerization

Effect of the polymerization temperature on the polymerization activity and the isotactic index of polypropylene were shown in Fig. 3. As we know, the increase of the polymerization temperature not only makes the polymerization rate constant increase but also decreases the solubility of propylene gas in the solvent. Just because the contrary influence of polymerization temperature on the two aspects, the maximum of the polymerization activity occurs at 25°C in Fig. 3. The increase of the isotactic index of the resultant polypropylene can be explained as: higher polymerization temperature may convert the single metal active center (structure 1, Fig. 4) to double metal active center and double metal active center (structure 2, Fig. 4) is liable to produce high isotactic polypropylene.

3.3. Effect of the Al/Ti molar ratio on the propylene polymerization

As Fig. 5 is shown, with the increase of the Al/Ti molar ratio, the polymerization activity firstly increases and then decreases, and the isotactic index of polypropylene increases all the while. The reason is that with the increase of the Al/Ti molar ratio, the Ti^{4+} is firstly reduced to Ti^{3+} which possesses the polymerization activity to propylene monomers. However, the excess of

the AlEt_3 may make Ti^{3+} further be reduced to Ti^{2+} , which is inactive to propylene monomers, and in turn the polymerization activity decreases. Meanwhile, as we know, single metal active center (structure 1, Fig. 4) is prone to produce the atactic polypropylene and double metal active center tends to produce the highly isotactic polypropylene [17]. Therefore with the increase of the Al/Ti molar ratio, the isotactic index of the resultant polypropylene increases because the conversion of structures 1–2 in Fig. 4.

As shown in Fig. 6, the speed of deactivation of the lower Al/Ti molar ratio is faster than that of the higher Al/Ti molar ratio. The results indicate that double metal active center (structure 2, Fig. 4) is more stable than single metal active center (structure 1, Fig. 4).

3.4. Effect of the external donor on the propylene polymerization

Addition of external donor, phenyltriethoxysilane, in the polymerization system has an adverse influence on the polymerization activity, as shown in Fig. 7. According to Kakugo [17], the MgCl_2 -supported Ti catalyst has two kinds of active centers, namely structures 1 and 3 in Fig. 8. As shown in Fig. 8, the addition of the external donor may convert nonstereospecific center to the high isospecific one (structure 2) and the low isotactic center to an inactive one [18]. Therefore with the increase of the Si/Al molar ratio, the isotactic index of the resultant polypropylene increases. And further increase of the Si/Al molar ratio may result in the reduction of the polymerization activity to a great content.

4. Conclusions

A low Ti-loading $\text{AlCl}_3/\text{MgCl}_2$ -supported Ziegler–Natta catalyst is prepared and low isotactic polypropylene is synthesized using this catalyst in the paper. The results indicate that the polymerization activity of the $\text{AlCl}_3/\text{MgCl}_2$ -supported Ziegler–Natta catalyst is much higher than that of the MgCl_2 -supported Ziegler–Natta catalyst. And the attenuation curves of the polymerization rate of different Al/Ti molar ratios suggest the double metal active center is more stable than the single metal active center.

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