Dependence of comonomer effect and hydrogen effect on internal donor in ethylene/1-hexene copolymerizations with MgCl₂-supported catalysts

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Abstract: Ethylene homopolymerization and copolymerizations with 1-hexene by three types of MgCl₂-supported catalysts were compared. Cat-1 contains no internal electron donor (ID), Cat-2 contains phthalic anhydride (PA) as ID, and Cat-3 contains anisole as ID. The influences of two kinds of ID on comonomer effect, the role of hydrogen, polymerization kinetics in ethylene/1-hexene copolymerization were investigated. The addition of ID improves the catalysts activities in ethylene polymerization. In comparison with ethylene homopolymerization, these ethylene/1-hexene copolymerization systems all showed strong comonomer effects. However, internal donor, especially anisole, weakens the extent of comonomer activity enhancement. When the concentration of 1-hexene is 0.6 mol/L, catalysts activities increase remarkably with adding a small amount of hydrogen. But, the addition of ID reduces the sensitivity of catalyst activity to hydrogen. The introduction of anisole increases the homo-polymerization rate rapidly at the initial stage, but makes it decay earlier. In ethylene/1-hexene copolymerization with hydrogen, the addition of phthalic anhydride as ID can stabilize the polymerization rate, but anisole accelerates the decaying trends. The results are discussed based on a kinetic mechanistic model of the ID effect on ethylene copolymerization.

Introduction

MgCl₂/TiCl₄ type supported Ziegler-Natta catalysts are widely used in industry for the production of polyethylene and polypropylene [1, 2]. They are usually prepared by contacting anhydrous magnesium chloride or its compounds with titanium tetrachloride. It has been well known that anhydrous MgCl₂ is the best support coordinated with TiCl₄ both in electron structure and crystal structure [1, 3]. Internal electron donor (ID) is an electron donating organic compound added to the catalyst during its preparation. The effect of ID on the propylene polymerization catalysts and polymer properties has been largely studied in the literature. An important role of ID in propylene polymerization is believed to be to improve the regioselectivity of catalysts and isotacticity of polypropylene [4, 5].

In recent years, many publications reported the copolymerization of ethylene with α-olefin [6-10]. However, there are very few references dealing with the roles of electron donors in the catalysts and the mechanism. We had found that ID can enhance the activity of TiCl₄/MgCl₂ supported catalysts. At the same time, ID affected the comonomer composition and chemical composition distribution (CCD) in
copolymers. Addition of phthalic anhydride (PA) as internal electron donor to catalysts may decrease the comonomer content in copolymers significantly, while addition of anisole increased the content slightly. Furthermore, the introduction of an internal donor to the catalysts, especially diethyl phthalate (DEP), increased the blockiness of n-heptane insoluble (HI) fractions [11].

Polymerization kinetics is one of key phenomena in olefin polymerization with heterogeneous transition metal catalysts. It will be of great significance to study the kinetics of polymerization for understanding the polymerization mechanism and designing polymerization technology in industry [12-14]. Many recent reports have been studying the nature of multicenters in supported Ziegler-Natta catalysts [15, 16]. The different centres kinetics responds differently to changes in olefin polymerization reaction. The polymerization kinetics was used to understand the effect of commoner and hydrogen on different centres in ethylene polymerization. However, there are very few researches dealing with the roles of electron donors on comonomer effect and hydrogen effect in ethylene copolymerization with α-olefin.

![Scheme 1. Structures of two kinds of internal donors.](image)

In the present article, two kinds of typical internal donors (PA and anisole) were employed. Catalysts for isospecific propylene polymerization usually contain diester compounds such as ID [5]. MgCl₂·nTHF adducts are often used to prepare supported catalysts suitable for ethylene-α-olefin copolymerization [17, 18]. This kind of catalysts actually contains THF as ID. In addition, the diester compound from reactant of PA and ethanol is a bidentate compound, while anisole is a monodentate compound, and some useful information would be achieved from the contrast of the two different kinds of internal donors.

Three types of TiCl₄/MgCl₂ type supported Ziegler-Natta catalysts were prepared. Cat-1 contains no ID, Cat-2 contains PA as ID and Cat-3 contains anisole as ID. In this work, ethylene/1-hexene copolymerizations catalyzed by MgCl₂/ID/TiCl₄ type supported Ziegler-Natta catalysts containing different ID were studied. Two kinds of internal donors, anhydride and ether, were compared for their influences on comonomer effect, the role of hydrogen and polymerization kinetics in ethylene copolymerization with 1-hexene. In particular, the kinetic mechanism for the effect of ID on homo- and copolymerization of ethylene was proposed.

**Results and discussion**

**Influence of internal donor on comonomer effect**

The results of ethylene homo-polymerization and ethylene/1-hexene copolymerization catalyzed by the three catalysts are shown in Figure 1. The introduction of internal donor in the catalysts led to a significant increase of catalyst
activity in ethylene polymerization, especially anisole. ID in catalysts may coordinate with active centres and enhance the stabilization of active centres and the catalysts activities [11].

Fig. 1. Effect of comonomer and internal donors on activities of ethylene/1-hexene copolymerization at 70 °C, [1-hexene]₀ = 0 and 0.6 M. Polymerization Conditions: Pₑ = 0.2 Mpa, TIBA, Al/Ti = 100, T_p = 70 °C, t_p = 10 min.

The experimental kinetic curves of ethylene homopolymerization with three catalysts are shown in Figure 2. It can be seen that the polymerization rates increase rapidly at the initial stage (within 10 min) decreasing later and the polymerization rate is enhanced sharply with a kind of ID at the early stage of polymerization. In the case of Cat-2 with PA as ID, the reaction is kinetically controlled and is relatively stable. Whereas, the activity of Cat 3 with anisole as ID grows sharply initially, and then it decreases to a steady state when maximal activity is attained.

In comparison with ethylene homopolymerization, these copolymerization systems all showed strong comonomer effects. As 1-hexene concentration was 0.6 mol/L, the catalyst activities increased markedly, especially in the case of Cat-2. Similar effects have been found in many heterogeneous Ziegler-Natta catalyst systems. The mechanism of comonomer effect is given in Scheme 2. As Kissin proposed, in ethylene polymerization, a large proportion of “sleeping” centres were immediately produced for the β-agostically coordinated Ti-C₅H₅ group and the coordination vacancy of Ti for ethylene was occupied by hydrogen atom, which reduced the activities of catalysts in ethylene homopolymerization reaction [19]. When α-olefin was introduced into ethylene polymerization, it inserted into the Ti-H bond with an immediate formation of Ti-polymer bond. Consequently, the activity in ethylene copolymerization was enhanced significantly.
Fig. 2. Kinetic profiles of ethylene homopolymerization with three types of catalysts in absence of hydrogen at 70 °C, P_E = 0.2 Mpa.

Scheme 2. Proposed kinetic mechanism of ethylene copolymerization reaction [19].

However, the addition of internal donors may influence the comonomer effect in ethylene copolymerization with 1-hexene. To evaluate the comonomer effect, activity increment is defined as:

\[
\text{Activity increment} = \frac{\text{Activity}_{\text{copolymerization}}}{\text{Activity}_{\text{homopolymerization}}}
\]

And it indicates the extent of activity enhancement during the same period of reaction time after the addition of comonomer. All these results are shown in Table 1. As seen from Table 1, addition of ID can weaken the extent of activity enhancement, especially anisole. In ethylene polymerization, the strong β-agostic interaction between C-H bonds of growing polymer chains and the Ti atoms causes a large proportion of low iso-specific active centres to turn to “sleeping” active centres [16, 19]. A plausible interpretation is that ID probably increases the concentration of the high iso-specific active centres, thus reducing the ability of incorporating α-olefin.

When 1-hexene is present, copolymerization kinetics of all the catalysts present the depressing tendency, as shown in Figure 3. Under the chosen reaction condition, the addition of ID can improve the catalyst activities substantially, especially for Cat-2. As expected, Cat-1 and Cat-3 with anisole as ID also have the same phenomena.
**Tab. 1.** Effect of 1-hexene on ethylene polymerization.

<table>
<thead>
<tr>
<th>Cat</th>
<th>Internal donor</th>
<th>[Ethylene] (mol/L)</th>
<th>[Hexene]₀ (mol/L)</th>
<th>Activity (KgPE/gTi·h)</th>
<th>Activity increment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-1</td>
<td>-</td>
<td>0.14</td>
<td>0</td>
<td>16.03</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14</td>
<td>0.6</td>
<td>65.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14</td>
<td>0</td>
<td>29.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PA (DEP)</td>
<td>0.14</td>
<td>0.6</td>
<td>99.20</td>
<td>3.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14</td>
<td>0</td>
<td>45.50</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>Anisole</td>
<td>0.14</td>
<td>0.6</td>
<td>77.00</td>
<td></td>
</tr>
</tbody>
</table>

Conditions: Al/Ti = 100, T_p = 70 °C, P_Ethylene = 0.2 MPa, t_p = 10 min, cocatalyst: Al(i-Bu)_3.

**Fig. 3.** Kinetic profiles of ethylene/1-hexene copolymerization with three types of catalysts in absence of hydrogen at 70 °C, P_E = 0.2 Mpa, [1-hexene]₀ = 0.6 mol/L.

**Effect of ID on copolymerization in the presence of hydrogen**

It is supposed that hydrogen is the most commonly used chain transfer agent in olefin polymerization, at the same time, it can change polymerization behaviours and properties of the products [20, 21]. The effect of hydrogen on ethylene polymerization is different from that on α-olefins polymerization. In general, hydrogen decreases the catalyst activity in ethylene polymerization but increases that in α-olefins polymerization. These similar effects have been found by many researches [22, 23]. As shown in Table 2, it is conceivable that the hydrogen effects in ethylene/1-hexene copolymerization will be different. When the concentration of 1-hexene is 0.6 mol/L, the catalyst activities in ethylene copolymerization increase remarkably with adding a small amount of hydrogen. Introduction of internal donor may influence the role of hydrogen on the catalyst activities in ethylene copolymerization with 1-hexene. To investigate the effect of hydrogen on catalyst activities, the change of activities in ethylene/1-hexene copolymerization with and without hydrogen is defined as:

\[ A_{H2}/A = \frac{\text{Activity (with Hydrogen)}}{\text{Activity (no Hydrogen)}} \]
The data are used to mirror the extent of activity variation with hydrogen at the same reaction time. As shown in Table 2, ID depresses the sensitivity of catalyst activity to hydrogen, especially for Cat-3 with anisole as ID.

**Tab. 2.** Effect of hydrogen on ethylene/1-hexene copolymerization

<table>
<thead>
<tr>
<th>Cat</th>
<th>[Ethylene] (mol/L)</th>
<th>[Hexene]₀ (mol/L)</th>
<th>H₂ (mL)</th>
<th>Activity (KgPE/gTi·h)</th>
<th>(A_{H₂}/A) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-1</td>
<td>0.14</td>
<td>0.6</td>
<td>0</td>
<td>38.17</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.6</td>
<td>100</td>
<td>63.77</td>
<td></td>
</tr>
<tr>
<td>Cat-2</td>
<td>0.14</td>
<td>0.6</td>
<td>0</td>
<td>64.80</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.6</td>
<td>100</td>
<td>94.98</td>
<td></td>
</tr>
<tr>
<td>Cat-3</td>
<td>0.14</td>
<td>0.6</td>
<td>0</td>
<td>44.00</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.6</td>
<td>100</td>
<td>59.46</td>
<td></td>
</tr>
</tbody>
</table>

*Conditions: Al/Ti = 150, m(cat) = 20 mg, T = 70°C, \(P_{\text{Ethylene}}\) = 0.2 MPa, \(t_p\) = 30 min; solvent: \(n\)-heptane, cocatalyst: Al(\(i\)-Bu)₃.

**\(A_{H₂}/A\) = Activity (with Hydrogen)/Activity (no Hydrogen)**

**Fig. 4.** Kinetic profiles of ethylene/1-hexene copolymerization with three types of catalysts in presence of hydrogen at 70 °C, \(P_E = 0.2\) Mpa, \([1\text{-hexene}]_0 = 0.6\) mol/L.

Two conclusions can be drawn from the kinetic profiles of ethylene/1-hexene copolymerization in the presence of hydrogen, as shown in Figure 4: (1) Hydrogen increases the polymerization activation rates at the starting state. (2) The effects of two kinds of internal donors on polymerization kinetics are different. The addition of DEP (PA) as ID can make the polymerization rates more stable. However, the polymerization rate of Cat-3, which contains anisole as ID, deactivates rapidly.

**Mechanism of the effect of ID on ethylene copolymerization**

Heterogeneous Ti-based catalysts, such as TiCl₃ and MgCl₂/TiCl₄ supported catalysts, are all multicentre catalysts, and the centres should function differently for different monomer. It has also been reported that the copolymerization ability of the
active centers depends on the oxidation state and stereospecificity of Ti active sites [24]. Kakugo et al. reported that nonstereospecific and syndiospecific active centres show higher activity toward ethylene than that of highly isospecific active centres, and the activity of low isospecific active sites toward ethylene is about twice that of the highly isospecific one [25].

According to the properties of active centres, copolymerization ability, stereoregularity and kinetics, the active centers of ethylene polymerization can simply be divided into two groups: high isospecific active sites and low isospecific active sites. The former have higher activities in ethylene homopolymerization and show stable kinetic curves. When the centres coordinate with ethylene, it is not easy for them to become dormant. The latter have low activities in ethylene homopolymerization, and deactivate rapidly. Most of them are dormant because of the strongly β-agostic interaction.

The addition of ID can improve the stereospecificity of active centres, increase the steric hindrance and diminish the amount of the dormant active centres, thus enhancing the reaction rate in ethylene polymerization. In ethylene/1-hexene copolymerization, the introduction of comonomer can increase the catalyst activities by activating plenty of dormant active centres. However, the addition of ID in catalysts can reduce the dormant active centres that can be activated. Consequently, the addition of ID decreases the extent of activity increase after the introduction of 1-hexene in ethylene polymerization.

As described above, when the initial concentrations of 1-hexene is higher than that of ethylene in the ethylene/1-hexene copolymerization, small amount of hydrogen can improve the catalyst activities dramatically. It can be assumed that hydrogen may activate many low isospecific active sites, which improves the catalyst activities dramatically and causes the polymerization kinetics decaying very quickly. As expected, the addition of ID also affects the kinetic curve of ethylene/1-hexene copolymerization in the presence of hydrogen. Diester type internal donor (like DEP in Cat-2) has strong capacity of complex formation and improves the stereo-regulating ability of active centres. A part of low isospecific active sites are transformed into isospecific ones by the internal donor, which may reduce the relative magnitudes of active centres activated by hydrogen and make the kinetics curve of ethylene/1-hexene copolymerization very stable. However, anisole exerted distinctly different effects on the catalyst as compared to DEP. This could be explained by weaker coordination ability of anisole than DEP, because anisole is a monodentate donor. Anisole cannot diminish the proportion of the low isospecific active sites activated by hydrogen and the profile of kinetic curve is similar to that of Cat-1 with an obvious depressing trend.

**Conclusions**

In conclusion, diester type and ether type internal donors played greatly different roles on catalyst activity, comonomer effect and hydrogen effect in ethylene polymerization catalyzed by TiCl₄/ID/MgCl₂ type Ziegler-Natta catalysts.

Firstly, the addition of ID improves the catalysts activities in ethylene polymerization. However, addition of ID weakens the extent of comonomer activity enhancement in ethylene/1-hexene copolymerization reactions.
Secondly, small amount of hydrogen can improve the catalyst activities dramatically when the initial concentration of 1-hexene is higher than that of ethylene. However, ID reduces the sensitivity of catalyst activity to hydrogen.

Finally, the addition of ID showed greatly different effects on polymerization kinetics in ethylene polymerization. The ethylene homopolymerization kinetics remains stable while the kinetic profiles of ethylene/1-hexene copolymerization become decaying in all cases. The introduction of anisole increases the polymerization rate rapidly at the initial stage, but leads to an earlier decay. In ethylene/1-hexene copolymerization with hydrogen, the addition of diester compound DEP as ID can make the polymerization rate more stable, but Anisole accelerates the decaying trends.

The experimental results are tentatively explained based on a kinetic mechanistic model, in which according to the properties of active centres, copolymerization ability, stereoregularity and kinetics, the active centers of ethylene polymerization can simply be divided into two groups and the addition of ID can affect the ratio of the two groups of active centres.

**Experimental part**

All reactions were carried out under nitrogen atmosphere.

**Preparation of the MgCl₂·nEtOH adducts and MgCl₂·nEtOH·ID adducts.**

4 g of anhydrous MgCl₂ (99%, Alfa Aesar) mixed with four equivalents of anhydrous ethanol (distilled and dried by 4 Å molecular sieve before using), a small amount of internal electron donor (ID) (phthalic anhydride or/and anisole) and 20 mL of anhydrous n-heptane were successively added into a flask. The flask was then heated to 120 °C and maintained for 6 h with magnetic stirring until the MgCl₂ was completely dissolved. Then the mixture was cooled to room temperature. The solvent and the unreacted ethanol were removed by evacuation, and the MgCl₂·nEtOH·ID adduct (Adduct-2, Adduct-3, Adduct-4) was collected as white powder. The dried adduct powder was sealed in a glass bottle and stored. MgCl₂·nEtOH adduct (Adduct-1) without addition of ID was prepared in a similar procedure.

The addition of PA in the preparation of MgCl₂·nEtOH·ID adduct led to the in-situ formation of diethyl (o-) phthalate (DEP). Therefore, DEP is the actual ID existing in the final catalyst prepared based on this adduct [11].

**Preparation of catalysts**

10 g of anhydrous MgCl₂·nEtOH (or MgCl₂·nEtOH·ID) adduct was added into a three-neck flask. Then a large excess of titanium tetrachloride (Ti/Mg = 20) was injected into the flask at -20 °C with magnetic stirring. The temperature was then raised to 120 °C and kept for 2 h. As the mixture was cooled to 60 °C, the liquid in the mixture was removed (siphoned off) and the remaining solid was washed twice with anhydrous n-heptane. Subsequently, a large excess of titanium tetrachloride was injected into the flask and mixed with the remaining solid. Then the mixture was kept at 120 °C for 2 h. Finally, the mixture was cooled to 60 °C and the liquid was removed. The remaining solid was washed six times with anhydrous n-heptane and then dried in vacuum. Thus, three catalysts (Cat-1, Cat-2 and Cat-3) were prepared and stored at -20 °C in a drybox.
Analysis of adducts and catalysts

FTIR spectra of adducts and catalysts were recorded on a Bruker Vector 22 FTIR spectrophotometer with a sample wafer mixed with KBr power.

The Ti content of the catalysts was determined by conventional spectrophotometry method [26]. Titanium content of the catalysts containing different internal donors is listed in Table 3.

<table>
<thead>
<tr>
<th>Cat.</th>
<th>ETOH/MgCl₂</th>
<th>Internal donor</th>
<th>ID/MgCl₂</th>
<th>Color</th>
<th>Ti content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-1</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>Beige</td>
<td>8.2</td>
</tr>
<tr>
<td>Cat-2</td>
<td>4</td>
<td>PA</td>
<td>0.1</td>
<td>Brown</td>
<td>4.4</td>
</tr>
<tr>
<td>Cat-3</td>
<td>4</td>
<td>anisole</td>
<td>0.2</td>
<td>Red-brown</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Polymerization

All of the polymerizations were carried out at 70 ℃ in a 0.5 L jacketed Büchiglasuster reactor which was evacuated and purged by N₂ three times and then filled with ethylene at 1 atm. 200 mL of n-heptane as solvent, a designated volume of 1-hexene and Al(i-C₄H₉)₃ (TIBA, Albemarle Co.) were successively added into the reactor. 20-30 mg of catalyst was added into the reactor to catalyze ethylene polymerization for 30-110 min. Ethylene at 2 atm was continuously supplied into the flask to maintain a constant pressure. At the end of polymerization, ethylene was stopped and the slurry was poured into 500 mL ethanol containing 2.5 mL hydrochloric acid to terminate the reaction and settling down the polymer. The polymer particles were filtered, washed with ethanol and dried in vacuum at 50 ℃.

Acknowledgements

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References