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External Donor Induced Direct Contact Effects on $Mg(OC_2H_5)_2$-Based Ziegler-Natta Catalysts for Propylene Polymerization

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Summary: Effects of external donor induced direct contact without alkylaluminum were studied for Ziegler-Natta catalysts containing monoester and diester as internal donors on the catalytic performances such as activity and stereoselectivity. Traditional slurry polymerizations were carried out for rather short period after direct contact for a variety of time. GC analysis was also performed to observe replacement phenomena of donors during direct contact. It was postulated that the different performances of the catalysts were greatly affected by the pair of internal and external donors.

Keywords: activation; direct contact; internal and external donors; propylene polymerization; Ziegler-Natta catalyst

Introduction

Advances in the technology of heterogeneous Ziegler-Natta catalysts have led to the production of a wide range of polypropylene.[1,2] Typical example of the Ziegler-Natta catalyst is a mixture of the $MgCl_2$-supported Ti-based catalyst and an alkylaluminum cocatalyst such as triethylaluminum or triisobutylaluminum.[3,4] A great variety of catalysts containing $MgCl_2$ as a support have been developed to use in the industrial process. $Mg(OC_2H_5)_2$ has been regarded as one of the best material to form $MgCl_2$-supported industrial polyolefin catalysts.

Investigation of many unsolved questions with respect to propylene polymerizations by Ziegler-Natta catalysts is still a meaningful research topic in both industrial and academic aspects. Especially, profound understanding of effects and roles of external donor has been regarded as a key factor for the development of new catalyst systems.[5] The presence of an internal donor used for catalyst preparation and an external donor added for a polymerization is indispensable for improving catalytic performances as well as polymer properties.[6–8] In fact, the effectiveness of the catalyst system is dependent on the choice of the specific pair of internal and external donors.[9] As an internal donor, EB (ethylbenzoate) was originally found to use in the industrial catalyst system, then DBP (n-dibutylphthalate) was discovered and most widely used in the present catalyst system combined with some specific silane compound.[10] The kinetic behaviors of the catalysts using those two types of the internal donors are known to be clearly different.[11] The EB containing catalyst shows very high initial activity with drastic decay, but the DBP containing catalyst has much milder kinetic feature, slow activation and relatively slow decay. These phenomena have been explained by the state and the effects of donors. It was demonstrated that an internal donor was strongly bound to the $MgCl_2$ support and

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did not interact with adsorbed $TiCl_4$.[12,13] In general, donors block aspecific sites on $MgCl_2$ surface selectively to increase the isospecific Ti dinuclear species and coadsorb with Ti species to transform aspecific sites into isospecific sites.[14–16] Even though many scientists explained isospecificity increase by the existence of donors according to these results, the effects of donors are considered to be more complicated.[17–19]

For the further improvement of the Ziegler-Natta catalyst system, it is essential to understand how donors interact with other components of the catalyst. The internal donor coordinated to the $MgCl_2$ surface is desorbed from the solid catalyst by the reaction with alkylaluminum.[20,21] In contrast, the external donor is adsorbed in the vicinity of at least some isospecific sites in such a way as to modify their stereochemical behavior or to generate new isospecific centers having different stereoselectivity.[22,23]

Recently, aminosilane compounds having dihydrocarbyl amino or cyclic amino groups were noticed because they presented very unique characteristics for the control of molecular weight and its distribution when they were applied to external donors.[24] Aminosilane compounds containing amino groups and alkoxy groups can interact with the catalyst through both nitrogen and oxygen atom.[19] Dihydrocarbyl amino and cyclic amino groups are structurally similar to sec-hydrocarbyl groups in a point that the secondary carbon atom is replaced by the nitrogen atom. However, the exact features of those compounds are not established yet. There is a close correlation between the polymerization performance and the amount of existing internal and external donors in the catalyst.[9] Even though these interactions among main components of the catalyst greatly affect catalytic performances, the exact mechanism of these phenomena is still ambiguous.[25] Especially, the direct interaction of the external donor to the catalyst has rarely been paid attention and effects of them on catalytic performances are questionable.

In this paper, the external donor induced direct contact effects on the activity and the isospecificity were investigated for the $MgCl_2$-supported Ziegler-Natta catalyst including monoester or diesta. A variety of external donors including monoester and silane compounds were employed from the view point of industrial interests.

Experimental Part

Materials

Propylene of research grade (donated by Japan Polypropylene Co.) was used without further purification. Ethylbenzoate (EB, purchased from Wako Pure Chemical Industries, Ltd.) and n-dibutylphthalate (DBP, purchased from Wako Pure Chemical Industries Ltd.) were dehydrated with molecular sieves before use. $Mg(OC_2H_5)_2$ (donated by Toho Catalyst Co. Ltd), $TiCl_4$ (purchased from Wako Pure Chemical Industries Ltd.), triisobutyl aluminum (donated by Tosoh Akzo Co.), cyclohexylmethyldimethoxysilane (Csi, donated by Ube Industries Ltd.) and bis(perhydroisoqunolino)dimethoxysilane (Qsi, donated by Ube Industries Ltd.) were used without further purification. Heptane was purified by passing through a column of molecular sieves.

Catalyst Preparation

The catalysts used in this paper were prepared by reaction of spherical $Mg(OC_2H_5)_2$ with $TiCl_4$ in the presence of EB or DBP using the procedure described in the USP 4,829,037. The catalyst without an internal donor was also prepared by the same procedure. In Table 1, the contents of Ti and internal donors of each catalyst are summarized.

Direct Contact and Polymerizations

Direct contact of the catalysts was carried out in a glass reactor at room temperature. The external donor (1.40 mmol) and the solid catalyst (0.467 mmol-Ti) were introduced into a glass reactor containing 100 ml of heptane as a solvent. After direct

Table 1.
Contents of Ti and internal donors of catalysts.

Catalyst	Content (wt.%)	
	Ti[a)]	Internal Donor[b)]
None	9.6	–
EB	3.3	13.0
DBP	2.6	16.0

[a)] Analyzed by a titration method.
[b)] Analyzed by GC.

contact, 20 ml of slurry was transferred into another flask containing 180 ml of heptane and triisobutylaluminum (2.8 mmol) and then polymerize propylene at 30 °C for 5 min under atmospheric pressure.

Polymerizations without direct contact were carried out in a glass reactor containing 200 ml of heptane. Triisobutylaluminum (2.8 mmol), the external donor (0.28 mmol) and the solid catalyst (0.0934 mmol-Ti) were introduced in the order to polymerize propylene at 30 °C for 5 minutes under atmospheric pressure.

The obtained polymers were analyzed by Flow Injection Polymer Analysis (FIPA) method to determine xylene insoluble content.

Gas Chromatography (GC) Analysis

After direct contact of the catalyst with the external donor through the method right above, the catalyst was suspended in heptane and then the upper solution was separated and analyzed by gas chromatography.

Results and Discussion

Table 2.
Polymerization activities and isospecificity of the catalysts with or without an internal donor[a)].

No.	Catalyst	External Donor	Activity[b)]	*mmmm*[c)]
1	None	EB	0.9	68.1
2		Csi	0.9	76.3
3		Qsi	1.0	72.9
4	EB	EB	13.6	87.7
5		Csi	9.3	91.4
6		Qsi	11.3	88.6
7	DBP	EB	3.9	80.0
8		Csi	3.5	94.3
9		Qsi	3.6	94.1

[a)] Slurry polymerizations in heptane with triisobutylaluminum (Al/Ti molar ratio = 30) and external donors (Al/donor molar ratio = 10) at 30 °C for 5 minutes under atmospheric pressure.
[b)] g-PP/mmol-Ti.min.
[c)] mol% (determined by ^{13}C NMR spectroscopy).

Table 2 shows the polymerization activities and isospecificity of the catalysts with EB or DBP as well as the catalyst without an internal donor. The results are greatly different for the catalysts. The low activity without an internal donor clearly indicates that the existence of an internal donor has an important role for establishing the catalyst performances. The EB containing catalyst has the highest activity reflecting its high initial activity as mentioned in the introduction. The Csi external donor presented the highest isospecificity particularly when it was combined with the DBP containing catalyst. It was confirmed that appropriate combination exists for the improvement of isospecificity in the pair of the internal donor and the external donor. For example, the EB external donor showed comparable isospecificity with Csi when it was combined with the EB containing catalyst while it was much less effective with the DBP containing catalyst.

Direct contact of the catalysts containing EB or DBP as an internal donor was performed using three different types of external donors to polymerize propylene with cocatalyst. The polymerization time was relatively short (5 min) to prevent the excess interaction among the catalyst components and the unfavorable changes of active sites during the polymerization. For comparison, the polymerizations without direct contact of the catalyst were also carried out.

Figure 1 shows the significant decrease of activity of the EB containing catalyst in the early stage of direct contact, while xylene insoluble contents indicated different trends depending on the external donor in Figure 2. In the case of external EB and Qsi, the contents decreased as direct contact time increased, while Csi showed slight increase after direct contact. The Qsi donor showed moderate levels in both activity and isospecificity. It was assumed

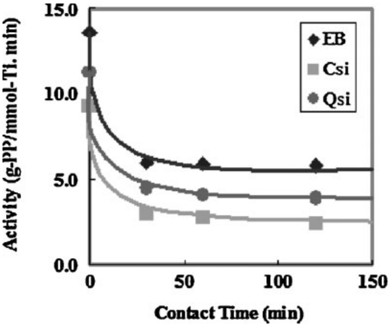

Figure 1.
Polymerization activities of the EB containing catalyst.

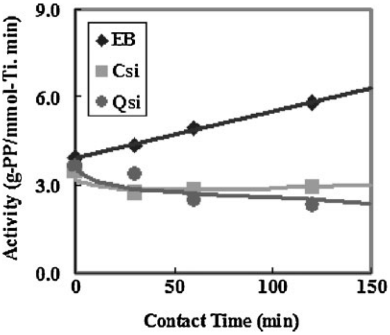

Figure 3.
Polymerization activities of the DBP containing catalyst.

that the drastic activity decrease is due to the difficulty of activation by alkylaluminum when the external donor is coordinated with the titanium species before the activation.[26] The external donor has been regarded to form a complex with alkylaluminum even in mild condition.[27] This complexation decreases coordination ability of the external donor to protect active sites from the deactivation. Therefore, the drastic activity decrease did not take place in the case of no direct contact. Another point is that there was almost no change of activity after direct contact for 30 minutes even enough amount of the external donor was present in the solution. The increase of isospecificity is thought to be driven by the stronger preferential interaction of Csi to convert the aspecific sites into more isospecific sites as well as by the stronger depression of the aspecific sites formation, resulting in the lower activity for the catalyst system with Csi.

Results of the propylene polymerization using the DBP containing catalyst after direct contact were shown in Figure 3 and 4. The DBP containing catalyst showed totally different activity trends from the EB containing catalyst. Activity of the EB external donor increased continuously as direct contact time increased and other external donors showed slight decrease. Whereas isospecificity trends of EB and Csi were as the same direction with those of the

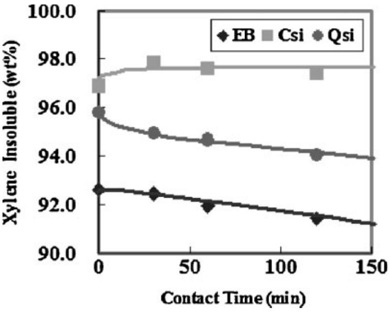

Figure 2.
Xylene insoluble contents of polymers obtained by the EB containing catalyst.

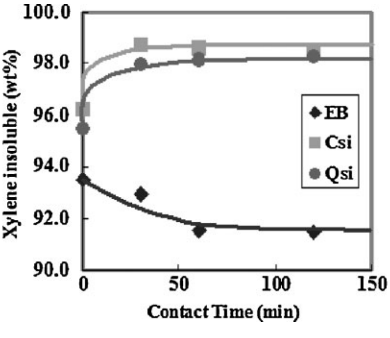

Figure 4.
Xylene insoluble contents of polymers obtained by the DBP containing catalyst.

EB containing catalyst, Qsi presented a different trend with that of the EB containing catalyst. It was observed that the Qsi showed the increase of isospecificity like Csi. Direct contact of EB to the DBP catalyst resulted in the increase of activity and the decrease of isospecificity. The DBP catalyst is activated more slowly than the EB catalyst as mentioned in the introduction. The replaced EB by direct contact induced the rapid activation of the catalyst and accelerates the whole polymerization. However, it is not the case of the Csi external donor.

These differences in trends of activity and isospecificity between the EB containing catalyst and the DBP containing catalyst can be assumed to be caused by the more stable coordination of DBP than EB because of its availability for bridging or bi-dentate coordination.

GC analysis was performed to observe adsorption and desorption phenomena of donors during direct contact. Direct contact of the catalyst with the external donor induced desorption of the internal donor and adsorption of the external donor as shown in Table 3. The desorbed amount of DBP was quite limited whereas considerably large amount of EB was desorbed. The differences of the contents between the EB and DBP internal donors in the upper solutions are also due to the fact that DBP can be bound more strongly than EB to the catalyst surface. Qsi was more effective to extract the internal donor from the solid catalyst and less effective to be adsorbed into the solid catalyst.

Table 3.
Contents of donors in the upper solution after direct contact analyzed by GC.

No.	Direct Contact		Content (%)	
	Internal Donor	External Donor	Internal Donor[a)]	External Donor[b)]
1	EB	Csi	21.9	50.4
2	EB	Qsi	34.9	55.5
3	DBP	EB	1.4	68.1
4	DBP	Csi	2.8	59.9
5	DBP	Qsi	8.4	72.6

[a)] Percentage of the desorbed amount from the solid catalyst.

[b)] Percentage of the remained amount in the upper solution.

Conclusion

It was postulated that the external donor induced direct contact effects significantly affected main catalytic performances significantly. Different performances of the catalysts including monoester or diester were found to be caused by the fact that diester can be bound more strongly. It was also confirmed that the appropriate combination of the internal and external donors was the key to achieve the preferable effects of direct contact.

The results of this study may give useful insights to understand the behavior and the relationship of internal and external donors and be helpful for the developments of more effective catalyst systems.

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