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Hydrogen Effects for Propylene Polymerization with Ultra Low $TiCl_3$ Loading $MgCl_2$-Supported Catalyst

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Summary: Hydrogen effects for propylene polymerization were investigated with ultra low $TiCl_3$ loading $MgCl_2$-supported catalysts in which the electric states of Ti species can be almost uniform. Hydrogen did not affect the catalyst activity, while the efficiency of hydrogen as a chain transfer agent was found to depend on the Ti content of the catalyst and the stereospecificity of the polymerization sites: Hydrogen was effective for isospecific sites independent of Ti contents, but inert for aspecific sites only at the extremely low Ti content. These results were explained within the island model, where isospecific sites may be located in the islands with other Ti species in their surroundings acting, as a steric hindrance for isospecific polymerization and as hydrogen dissociation sites after deactivation. Most of the aspecific sites should be isolated only at the extremely low Ti content. These isolated sites have no other Ti species in their surroundings, i.e. no hydrogen dissociation sites, and are inert to hydrogen.

Keywords: chain transfer; polypropylene (PP); ziegler-natta catalyst

Introduction

Ziegler-Natta catalyst is one of the most important discoveries in the chemical field during last century for its successful syntheses of polyolefins at low pressure and temperature.[1] Highly isotactic polypropylene (PP) has been achieved based on successful development of electron donor (ED) compound.[2,3] ED also affects the response to hydrogen,[4] which has been used as a chain transfer agent for precise control of the molecular weight of polymer in all industrial processes.[2] However, higher amount of hydrogen in PP plant reactor usually decreases its production level. In order to overcome this problem, more detailed understanding of the hydrogen acting mechanism has been regarded as the most important subject.[5,6]

In a series of our studies, the hydrogen effects were investigated with the stopped-flow technique, by which the chain transfer reactions by Al-alkyl cocatalyst or monomer could be negligible and quasi-living polymerization can be realized within an extremely short polymerization period (ca. 0.2 s).[7–9] Surprisingly, hydrogen was effective as a chain transfer agent only when some of active sites were deactivated by triethyl aluminum (TEA). This phenomenon could be explained by the transformation of polymerization sites into hydrogen dissociation sites.

However, the relationship between the existing states of surface Ti species and hydrogen effects has never been investigated. Because the ‘‘spillover’’ of hydrogen atoms has never been reported on metal halide like $MgCl_2$, it remains unresolved how they access from the hydrogen dissociation sites to polymerization sites. In the previous reports by Terano et al.[10] and Shiono et al.[11] with an ultra low $TiCl_3$ loading supported catalyst, it was found that the catalysts had low stereospecificity and that the response to hydrogen depended

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on the stereospecificity of the active sites. These results suggest the importance of the surroundings around polymerization sites on hydrogen induced chain transfer reaction.[12]

The objective of this study is to investigate the relationship between the existing states of the surface Ti species and hydrogen effects on propylene polymerization using the catalysts having different Ti contents.

Experimental Part

Materials

Heptane, propylene, hydrogen and nitrogen were used after passing through a molecular sieves 13-X column. Anhydrous $MgCl_2$ with a surface area of 65.1 m^2/g, $TiCl_3$ (T-type, Toho Catalyst Co.), TEA and DEAC (Tosoh Finechem Co.) were used without further purification.

Catalyst Preparation

$MgCl_2$-supported $TiCl_3$ catalyst was prepared according to the procedure reported in the previous paper.[10] $TiCl_3$ of 4 g was reacted with 20 ml of pyridine (Py) at room temperature under stirring in nitrogen for 8 h. Reaction product was washed adequately with heptane and dried in vacuo to obtain $TiCl_3 \cdot 3Py$ complex. $MgCl_2$ of 5 g and $TiCl_3 \cdot 3Py$ complex of 500 mg were placed in a flask under nitrogen. DEAC of 45 mmol in heptane was introduced into the flask and stirred at room temperature for 3 h, then washed adequately with heptane to obtain Cat-A. Cat-B was prepared by the same procedure as Cat-A except using 10 g of $MgCl_2$, 20 mg of $TiCl_3 \cdot 3Py$ complex and 1.8 mmol of DEAC. It was reported that all Ti species supported had almost the same existing state in the catalyst, which was confirmed by ESR spectra having only one sharp signal with a g-value of 1.94.[10]

Polymerization

In 1 L stainless steel reactor equipped with magnetic stirrer, 600 ml of heptane, 1.09 mmol of TEA, measured amounts of catalyst corresponding to Al/Ti molar ratio 430 and hydrogen were introduced under propylene at 65 °C to start polymerization. Propylene was continuously introduced to keep the pressure at 0.8 MPa during polymerization. Polymerization was terminated after 1 h by adding 5 ml of ethanol. The reaction mixture was filtrated in order to divide the solid and the liquid parts. Solid part was dried under vacuum to obtain isotactic polymer. Liquid part was poured into an excess amount of ethanol to solidify atactic polymer, and also dried under vacuum.

Analytical Procedures

The Ti content of catalyst was determined by ICP (Jobin-Yvin, JY46P). The molecular weight of polymer was measured by GPC (Waters Associates, ALC/GPC 150C) with polystyrene columns (Showa Denko K. K., AD806M/S) at 140 °C using *o*-dichlorobenzene (ODCB) as the solvent.

H_2-D_2 Exchange Reaction

The H_2-D_2 exchange reaction was carried out to confirm the hydrogen dissociation ability of the catalyst according to the procedure reported in the previous paper.[9] H_2 and D_2 were used without purification. The measured amount of Cat-B (0.042 mmol of Ti) was placed in a flask. TEA of 1.5 mmol and 30 ml of heptane were introduced into the flask at room temperature. After the flask was fully evacuated, 150 ml of H_2 and 150 ml of D_2 were charged. After 5 min, 0.5 ml of gas sample was syringed out from the flask and analyzed by GC (J-Science LAB, GC7000HN with hydroisopak column).

Results and Discussion

The $MgCl_2$-supported $TiCl_3$ catalysts were prepared by treating $TiCl_3 \cdot 3Py$ complex with DEAC in the presence of $MgCl_2$. Catalysts with Ti species having almost same interaction with $MgCl_2$ could be achieved by this method.[10] Cat-A and Cat-B had Ti contents of 9.2×10^{-1} and

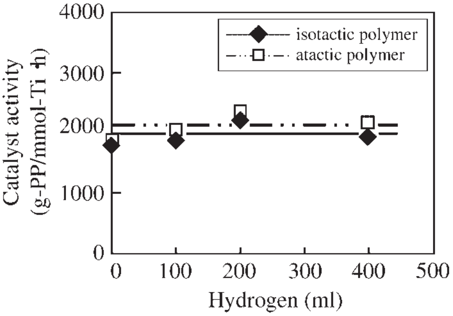

Figure 1.
Effect of hydrogen on catalyst activity with Cat-A.

1.8×10^{-2} wt%. The latter is extremely low with respect to general catalysts with typically around 3 wt%.

Figure 1 shows the relationship between the amount of hydrogen and catalyst activity of Cat-A to produce isotactic and atactic polymers, respectively.

Catalyst activities for isotactic polymer and atactic polymer are almost constant with various amount of hydrogen. The same tendency was obtained with Cat-B.

Figure 2 shows the relationship between the amount of hydrogen and molecular weights of isotactic polymers obtained with Cat-A or Cat-B.

The molecular weight of isotactic polymer is decreased by increasing the amount of hydrogen. Because the decrease of molecular weight by hydrogen is larger with Cat-A than with Cat-B, the hydrogen is more effective for higher Ti content. The molecular weight without hydrogen also depends on the Ti contents, which implies the propagation rate constant, k_p, is higher at higher Ti content.

Figure 3 shows the relationship between the amount of hydrogen and molecular weights of atactic polymers with Cat-A or Cat-B.

The molecular weight of atactic polymer obtained with Cat-A is decreased by increasing the amount of hydrogen as well as that of isotactic polymer. However, the molecular weight of atactic polymer obtained with Cat-B is almost constant with various amounts of hydrogen. In this case, hydrogen was found to be inert as a chain transfer agent.

For the further discussion on the results, the hydrogen dissociation ability of Cat-B was investigated through H_2-D_2 exchange reaction according to the previous report.[9]

As shown in Figure 4, the presence of HD in the GC chart confirmed that there were hydrogen dissociation sites in Cat-B.

The results Figure 2–4 can be explained by the "island model" as follows.[7,13]

Ti species are thought to exist in various distribution states on $MgCl_2$ surface, some of them are isolated and the others coagulate to make islands. Electric states of Ti species used in this study can be almost uniform, which is supported by the sole sharp signal of ESR spectra reported by Terano et al.[10]

Because the spillover of hydrogen atoms has never been reported on metal halides like $MgCl_2$, the hydrogen dissociation sites

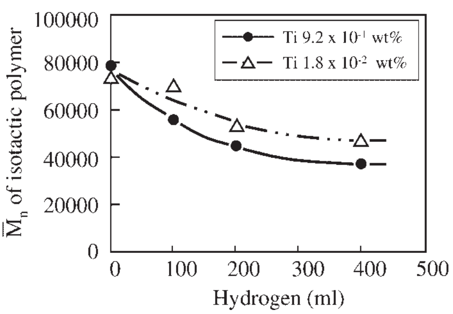

Figure 2.
Effect of hydrogen on molecular weight of isotactic polymer.

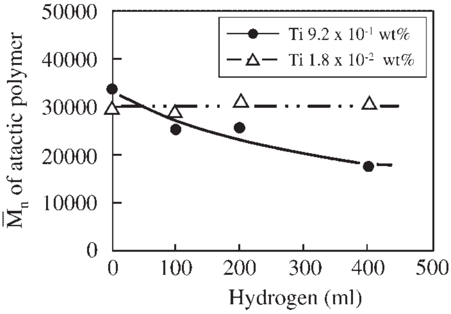

Figure 3.
Effect of hydrogen on molecular weight of atactic polymer.

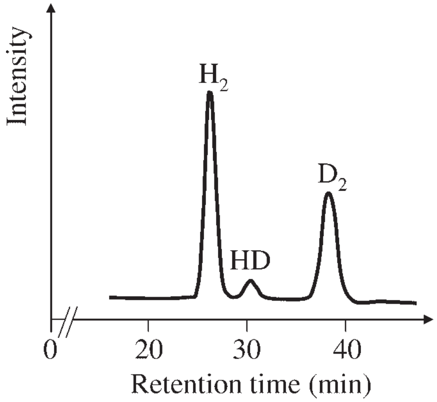

Figure 4.
Gas composition after H_2-D_2 exchange reaction with Cat-B.

are necessary in the instant neighborhood of the polymerization sites in order to make the hydrogen induced chain transfer reaction occur. Furthermore, some of the polymerization sites are transformed into the hydrogen dissociation sites by Al-alkyl.[7] Therefore, the hydrogen induced chain transfer reaction should occur inside one island, in which both the hydrogen dissociation sites and polymerization sites can be closely located. On the contrary, the isolated Ti species which make atactic polymers at the extremely low Ti content have no other Ti species in their surroundings. They are insensitive to hydrogen.

As shown in Figure 3, aspecific sites in Cat-B are insensitive to hydrogen in terms of the chain transfer reaction. On the other hand, Cat-B also has the hydrogen dissociation sites, which was confirmed by the production of HD in H_2-D_2 exchange reaction as shown in Figure 4. Thus, there should be ispspecific sites, aspecific isolated sites, and hydrogen dissociation sites in Cat-B. Nevertheless, the hydrogen atoms produced on the hydrogen dissociation sites reacted with the growing polymer chains only at the isospecific sites. Therefore, the aspecific sites in Cat-B should be isolated. This is in line with the concept that aspecific sites have less steric hindrance around them for recognizing the prochiral propylene face. On the contrary, isospecific sites independent of the Ti contents should be located in the islands in which polymerization sites have other Ti species in their surroundings. These Ti species can act as steric hindrance for isospecific propagation. Shiono et al. also reported the stereospecificity dependence of the similar catalysts on the Ti contents.[11] Stereospecificity was found to decrease as decreasing the Ti content.

Many isolated Ti species as well as rather small islands should be produced if an extremely low Ti content such as in Cat-B is employed. Therefore, most of the aspecific sites in Cat-B are considered to be isolated and inert to hydrogen. On the other hand, hydrogen is effective for isospecific sites in Cat-B because they are located in the islands even though their sizes are small. Many larger islands as well as a smaller number of isolated Ti species should be produced if a high Ti content such as in Cat-A is employed. Then, not only isospecific sites but also some aspecific sites are located in the islands. Therefore, hydrogen was effective for both isospecific and aspecific sites in Cat-A. The difference in the efficiency of hydrogen between Cat-A and Cat-B can be explained by the difference in the size of islands. Polymerization sites in the larger islands might have more other Ti species which can be transformed into hydrogen dissociation sites. Therefore, hydrogen can be more effective in the catalyst with the higher Ti content.

Conclusion

Hydrogen effects for propylene polymerization were investigated with ultra low $TiCl_3$ loading $MgCl_2$-supported catalysts. Hydrogen was effective as a chain transfer agent for the isospecific sites independent of Ti contents, but inert for the aspecific sites if the Ti content was extremely low. These results were discussed using the island model. The isospecific sites may be located in the islands with other Ti species in their surroundings which can act as a steric hindrance for isospecific propagation and can be transformed into hydrogen dissociation sites. Most of the aspecific sites should be isolated only when the Ti content is extremely low. These isolated sites have no other Ti species in their surroundings, i.e. no hydrogen dissociation sites, and therefore insensitive to hydrogen. Thus we successfully correlated the existing states of Ti species with their hydrogen response on the basis of the island model.

The results in this work are quite important and useful to improve the effect of hydrogen in the industrial propylene polymerization. Moreover, this work opened the possibility for the independent control of the molecular weights of isotactic and atactic polymers, which may contribute to the future developments of highly advanced polypropylene materials.

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