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Kinetic Analysis of Formation and Transformation of Stereospecific Active Sites on MgCl₂-Supported Ziegler-Natta Catalysts

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The large-scale increasing production of PP has been significantly enhanced by the development of highly efficient Ziegler-Natta catalysts. In spite of great research efforts in this field, a level of the mechanistic understanding of these catalysts has been far from satisfactory. Particularly, the topics concerning the formation mechanism and nature of stereospecific active sites as well as the polymerization mechanism are still open for discussion, even though the nature of the active sites plays a crucial role in determining catalyst performance.

The use of an Al-alkyl co-catalyst as an activating agent is indispensable for olefin polymerization with Ziegler-Natta catalysts. Al-alkyl cocatalyst is participating also in deactivation and transformation of the active sites during the polymerization. Whereas, the specific mechanism on how the cocatalyst affects the formation process and physicochemical feature of stereospecific active sites has remained ambiguous. Stereospecific active sites stemmed from the catalyst substrate, internal donor and cocatalyst, respectively, on the catalysts have never been differentiated because these factors will surely result in the successive change of nature and distribution state of stereospecific active sites in the whole polymerization process. Therefore, the achievement of further information on the specific stereochemical role of these factors and the mechanism of formation and transformation of the active sites will be useful in developing the PP as a new generation material.

The objective of this study is the elucidation of the formation and transformation of the stereospecific active sites on Ziegler-Natta catalysts caused by the interaction with cocatalyst. This study has the following two approaches.

- 1) Stopped-flow propene polymerization combined with TREF analysis
- 2) Development of temporal analysis of products (TAP) system and its application to research on Ziegler-Natta catalysis

In the first approach, stopped-flow propene polymerizations using MgCl₂-supported Ziegler-Natta catalysts pretreated by TEA cocatalyst within a short period of time were utilized as model reactions for probing the mechanism concerning the dynamic successive formation, deactivation and transformation of stereospecific active sites on the catalyst during the polymerization process. The formation of active sites with broad isospecificity distribution on this catalyst without pretreatment was found to be an ultra-fast reaction, and the active sites formed with higher isospecificity were more stable in the deactivation during the pretreatment. Based on the estimation of kinetic parameters and TREF analysis, a modified three-sites model with precise description of the stereospecific nature of various types of active sites stemmed from surface titanium species, Al-alkyl compounds, Mg-compounds and internal donors has been proposed. It was demonstrated that the isospecificity of active sites strongly depends on the bulkiness of the ligands situated at the two most important ligand positions for construction of asymmetry and chirality of the active sites with steric hindrance. In general, there may exist both monometallic and bimetallic sites in heterogeneous Ziegler-Natta catalyst system. The kinds of active titanium species with different chemical structures on this catalyst system should be limited, whereas, the non-discrete distribution of isospecificity of active sites could be considered to generate from the numerous types of steric and electronic effects from the surroundings of active titanium species as well as large number of reversible and dynamic transformation reactions simultaneously occurred on the heterogeneous catalyst surface.

In the second approach, a novel analytical equipment 'TAP' having submillisecond time resolution for investigation of Ziegler-Natta catalysis was developed. Mass resolution and gas transport condition which are needed for analysis of Ziegler-Natta catalysis were attained to enough level. The products generated from the reaction of TiCl₃ and TEA cocatalyst could detect by using TAP system. Thus, it turned out that TAP system is a very useful tool for investigation of Ziegler-Natta catalysis.

The findings obtained from this dissertation will be useful in developing the novel catalyst which can produce the new generation polyolefin materials.