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Kinetic and Morphological Investigation of Active Sites for Propylene Polymerization with Different MgCl_2 Supported Ziegler-Natta Catalysts

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Production of polyolefins becomes more than one hundred million tons/year over the world, which dominantly relied on heterogeneous Ziegler-Natta catalyst. After discovery of MgCl_2 as support material, the catalyst performances have been developed by finding new donor and improving the catalyst preparation method. Even these two factors, donor and catalyst preparation method, would affect at both particle and active site scales, many studies have been focused on either particle scale or active site scale separately. However it is important to design collectively considering from both particle and active site scales for total understanding and new development of catalyst. That is, development of new “catalyst preparation method” base on both particle and active site scale is key factor for design of next generation catalyst. The catalyst preparation method is known to affect the structure and the properties of catalyst, even though all the procedures give the same catalyst composition as $\text{TiCl}_4/\text{InD}/\text{MgCl}_2$. Nevertheless, it is still unclear how preparation method with a variety of internal donors, which is one of the component of solid catalyst, affects the important factors of catalyst structure for catalyst design, catalyst morphology, spatial distribution of Ti species, and active site nature, to lead to specific catalyst performance.

The objective of this dissertation is to clarify the effects of catalyst preparation methods with various internal donors for catalyst structure at both particle and active site scale aspects, namely morphology, active sites nature and their dispersion in the particle. In terms of both kinetic and morphological aspects, traditional grinding and advanced chemically activated catalyst were used and weighed for this purpose. Direct SEM observation and PSD development of the original catalyst and their produced polypropylene particles were used for morphology investigation, and the stopped-flow polymerization technique in combination with crystallinity distribution analysis of obtained polymers was used for kinetic analysis, respectively.

This dissertation consists of the following five chapters to discuss the effects and the role of catalyst preparation methods for propylene polymerization on the catalyst structure by morphological and kinetic investigation. The first chapter is general introduction according to the objective of this study. Effects of spatial distribution of active Ti species in the particles for polymerization kinetics and polymer morphology are discussed in chapter 2. Kinetic study for relationship between catalyst preparation method and active site nature is discussed in chapter 3. Effects of internal donor on active site nature and particle morphology of different MgCl_2 supported catalyst are discussed in chapter 4. Finally, general conclusion is described in chapter 5.

In this dissertation, it was shown that the polymer particle morphology and their growth were controlled by spatial distribution of active Ti species in the catalyst particle, which was different among catalyst preparation methods, even polymer morphology directly depends on the original catalyst particle generally. Moreover, the catalyst preparation method with each internal donor hardly affects the molecular structures of active sites, but affects the existing ratio of the kinds of active sites in the particle. On the other hand, the internal donors dominantly affected the active sites nature. As a result, combination of these two factors gives specific catalyst performances, leading to the variation of polymer properties. Additionally, it was found that the high performance of chemically activated catalyst originates from uniform spatial distribution of active Ti species in all over the catalyst particles to successfully control the initial fragmentation process and subsequent stable growth of the polymer particles, and the higher ratio of higher isospecific active site leading to totally higher isotactic polymer.

The results in this work are very important and useful to get clear understanding of the effects of the catalyst preparation method at both macro- and microscopic aspects, leading to the specific catalyst structure. This finding would contribute to the development of novel catalyst preparation method and the control of catalyst high-order structure. Furthermore, the finding will be also quite useful for the development of next generation Ziegler-Natta catalyst including process compatibility by the total design of the active site and the particle.