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Model Catalyst Approaches from Support and Active Species for Understanding of Ziegler-Natta Catalysis

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Polyolefin such as polypropylene and polyethylene produced with Ziegler-Natta catalysts is one of the largest markets. Research about the nature of Ziegler-Natta catalysts is ongoing because of the industrial importance for development of new grades of PP. $MgCl_2$-supported Ziegler-Natta catalysts consist of $TiCl_4$, $MgCl_2$, donors, triethylaluminum and H_2. Active sites of Ziegler-Natta catalysts are generally expressed by Ti species situated in an octahedral symmetry as a result of adsorption on unsaturated $MgCl_2$ surfaces. Donors interact with the Ti species in a non-bonded manner through co-adsorption on $MgCl_2$ surfaces. The catalytic nature of Ti species can be switched even during the elongation of one polymer chain due to ligand removal or exchange. These molecular-level understanding of surface events have been gradually established as a result of huge knowledge. However, there is still limited understanding of the nature of Ziegler-Natta catalysts because their surfaces are (more or less) chemically and structurally heterogeneous. The heterogeneity has inhibited the direct characterization of active sites, the evaluation of the catalytic performance of each active site, and the understanding of molecular-level behaviors of the catalysts. One of the helpful ways to address problems of the multisite nature is to employ using model catalysts which can reduce heterogeneity. The object of this dissertation is to develop novel Ziegler-Natta model catalysts which are useful to clarify active site natures.

In Chapter 2, polymerization properties and active site formation of various $MgCl_2$-supported titanocene catalysts were systematically investigated. Cp_xTiCl_{4-x} (x = 2-0) was immobilized on $MgCl_2$ by physical co-grinding or by chemical treatment with triethylaluminum (TEA). The obtained catalysts are designated as $Cp_xTiCl_{4-x}/MgCl_2$(P and C). Propylene polymerizations were conducted in the presence of TEA or modified methylaluminoxane (MMAO). $Cp_2TiCl_2/MgCl_2$(P, C) and $CpTiCl_3/MgCl_2$(C) produced mostly atactic PP in the presence of MMAO, similarly to the unsupported titanocene. On the other hand, the usage of TEA led to relatively isotactic PP, irrespectively of the employed precursors, indicating the active site nature quite similar to that of $TiCl_4/MgCl_2$. The supported titanocene catalysts offered both titanocene-type and Ziegler-Natta-type active sites natures according to the details of the preparation and the activation procedures. The observed dual active site natures were plausibly correlated with the valence and charge states of the Ti center. Novel dual active site natures which can be switched by the kind of activator were obtained. Molecular weight distribution became narrow with increase in the number of Cp ligands. However, active sites nature of $MgCl_2$-spported titanocene catalysts was more or less heterogeneous due to surface structure of $MgCl_2$ support.

In Chapter 3, in order to synthesis active $MgCl_2$ surface having homogeneous structure, $MgCl_2$ film was prepared by donor-induced surface reconstruction under ultra-high vacuum condition. $MgCl_2$ deposited on single-crystal metal substrates was always exposed the (001) surface irrespective of their surface symmetry, which does not allow the adsorption of donors under usual UHV conditions. $MgCl_2$·donor adducts are formed when $MgCl_2$ film is exposed to the vapor of a donor at a nearly saturated vapor pressure. While the desorption of a donor at a mild temperature leaves coordinative vacancies for $MgCl_2$ film, the introduction of a donor readily reconstruct the film structure into equilibrated one at a given environment (temperature, pressure). Thus, $MgCl_2$ structure is highly flexible in the presence of coordinating molecules, which seems to kinetically accelerate the reconstruction of $MgCl_2$. Moreover, a synthetic route for active $MgCl_2$ surfaces has been established by donor-induced reconstruction in UHV experiments. Obtained $MgCl_2$ film is a promising precursor toward the preparation of realistic Ziegler-Natta model surfaces in UHV.

The results in this study are remarkably important for development of useful model catalyst. The knowledge obtained in this study will contribute to the further development of the $MgCl_2$-supported Ziegler-Natta catalysts and the unique materials with improved properties.

Key Words: Ziegler-Natta model catalysts, $MgCl_2$-supported titanocene, dual active sites nature, ultra-high vacuum system, surface reconstruction