Title	モノ-，ジ-オレフィンのストップフロー重合とin situ固体NMR観察を組み合わせたオレフィン重合触媒の研究
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Stopped-Flow Polymerization of Mono- and Di-olefins Combined with *in situ* Solid-State NMR Observation for the Study of Olefin Polymerization Catalysis

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$MgCl_2$-supported Ziegler catalysts are now widely used in industry. However, the understanding of fundamental matters concerning the active sites has progressed more slowly than the commercial development of the catalysts, even though the nature of the active sites plays a crucial role in determining catalyst performance.

The objective of this study was the elucidation of the nature of the active sites on an $MgCl_2$-supported Ziegler catalyst. The concept was to examine from all aspects of the catalyst, the reaction and the polymer for olefin polymerization catalysis. This study had the following two approaches.

a) Enantio- and diastereo-selective olefin polymerization using the stopped-flow method
b) Development of *in situ* solid-state NMR investigations under continuous-flow conditions and its application to research on Ziegler-Natta catalysis

The first approach was based on the fractionation of the resulting polymers using TREF, combined with the stopped-flow polymerization technique. The TREF analysis of the polymer obtained by the stopped-flow method was thought to provide reliable information on the active sites just after formation. The microstructures of each fraction eluted at different temperatures were analyzed by ^{13}C NMR, suggesting the existence of the continuous distribution of the active sites having different selectivities for insertion and cyclization. Furthermore, the influence of internal and external donors was examined by the estimation of kinetic parameters and TREF analysis. Because the addition of the internal donor caused an obvious change in one of the kinetic parameters and the microstructure, an isospecific active site was found to be surely formed by the addition of the internal donor. In the case of the external donor, the additive effects on the stereospecificity were weaker than those of the internal donor. It was revealed from TREF measurements that the external donor modified an aspecific active site into a lower isospecific active site. In addition, the novel block copolymer having a chemical link between the PP part and the copolymer part containing the cyclic unit of 1,5-hexadiene was synthesized by modified stopped-flow method with the $MgCl_2$-supported Ziegler catalyst. The analysis of the copolymer part in the block copolymer was applied to gain additional insight into the nature of the active sites as well as the homopolymerization of 1,5-hexadiene. As a result, it was suggested that the high steric hindrance exists in the vicinity of isospecific active sites, and the low steric hindrance exists in the vicinity of aspecific active sites.

In the second approach, a new technique for the continuous monomer flow into the MAS rotor was first developed, which allowed the *in situ* NMR spectroscopic investigations of the transformation of the monomer to the polymer on a heterogeneous supported Ziegler catalyst. The important advantage of this technique was the ability to achieve the combination of quantitative information about the real time dynamics of the polymerization and the insight into the transformations of the active sites under actual reaction conditions. The *in situ* NMR technique under continuous-flow conditions combined with multinuclear (^{13}C, ^{1}H, ^{27}Al) high resolution solid-state NMR was applied to the investigation of the Ziegler-Natta catalyzed polymerization. As a result, the time-dependent change in the spectral peak intensities during the propene polymerization with the catalysts was measured using ^{13}C CP MAS (cross polarization with magic angle spinning) NMR and ^{1}H MAS NMR. The states of the aluminum complex in the catalysts were studied using ^{27}Al NMR, which is sensitive to the coordination and symmetry of the local environment around the aluminum nuclei. Peculiarities of the polymerization kinetics, the crystalline states of the nascent polypropene formed on the catalyst surface, and the state of aluminum coordination and environment during the early stage of the propene polymerization under continuous-flow condition were discussed. Furthermore, the activated supported catalysts after *in situ* polymerization of ethene, propene and 1,5-hexadiene were analyzed by ^{27}Al MAS NMR. The ^{27}Al MAS NMR spectra were similar to the ^{27}Al MAS NMR spectrum before the polymerization. Thus, it is assumed that the polymerization of mono- and di-olefins proceeds with the same polymerization mechanism because the states of the surface Al species on the $MgCl_2$-supported Ziegler catalyst were almost in agreement for all kinds of monomers.

Two approaches were carried out to investigate the nature of the active sites on the $MgCl_2$-supported Ziegler catalysts in this dissertation. These approaches were excellent for studying the active sites. From the results obtained by these approaches, the additional insight into the active sites was achieved, which could not be obtained from the conventional experimental methods. The findings obtained from this dissertation will be useful in developing the polyolefin as new generation material.