

Title	アルキルアルミニウムで活性化したフィリップス型触媒によるエチレンとシクロペンテンの重合に関する反応論的研究
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## Mechanistic Investigation on Ethylene and Cyclopentene Polymerizations Using Alkylaluminum Activated Phillips Type Catalysts

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Phillips  $\text{CrO}_x/\text{SiO}_2$  catalyst is well known as one of the most important industrial ethylene polymerization catalysts. Compared with Ziegler-Natta and metallocene catalysts, Phillips catalyst shows unique polymerization behavior, and its products have many unique chain microstructures, such as long chain branching, unsaturated chain end and ultra-broad molecular weight distribution, which contribute to excellent properties for both processing and final applications. Despite continuous and extensive research for more than half a century from the early 1950s, there is still very limited understanding of why Phillips catalyst has such unique behaviors. In general, the states of the active sites and the polymerization mechanism still remain unclear. The objective of my PhD research was to shed new light on these problems by investigation of the nature of the active sites and polymerization mechanism of the Phillips catalyst, and to develop further efficient catalysts for the synthesis of new polyethylene products.

First, a systematic investigation on the effects of Al-alkyl cocatalysts on ethylene polymerization was carried out. Introduction of a metal-alkyl cocatalyst at different stages (from catalyst preparation to polymerization) using Phillips catalyst can significantly affect active site formation, polymerization kinetics and polymer microstructure. The polymerization kinetic curves using PC600/TEA catalyst systems seemed to indicate a hybrid type, comprised of two types of basic polymerization kinetics: one is a fast formation and fast decay type and the other is a slow formation and slow decay type. This indicates the existence of two types of polymerization active sites. However, the polymerization kinetic curves using PC600/DEAE catalyst systems could indicate a typical single type polymerization kinetics, indicating only one type of polymerization site. This type of site can be ascribed to Cr(II) species coordinated with Al-alkoxy formed in two ways. Plausible mechanisms of the formation and transformation of active sites were proposed to rationalize the unique polymerization kinetics and microstructures of polymers in terms of short chain branches (SCBs), molecular weight (MW) and bimodal molecular weight distribution (MWD). These results will contribute to wider application of Phillips catalyst to traditional processes.

Second, calcined Phillips  $\text{CrO}_x/\text{SiO}_2$  catalyst (PC600) was adopted for the first time to catalyze copolymerization of ethylene and cyclopentene. Promotion effect of the cyclopentene co-monomer on ethylene polymerization activity was observed with increase of cyclopentene concentration. The activation effect of cyclopentene was assumed to be mainly responsible for the promotion effect on ethylene polymerization activity. Furthermore, the introduction of cyclopentene improved the properties of the resulting polymers. Moreover, this finding about copolymerization of ethylene and cyclopentene has also led to a breakthrough in the investigation of the polymerization mechanism. Because of the absence of internal C=C double bonds in the copolymer main chain, ring-opening metathesis polymerization of cyclopentene was excluded at the copolymerization stage of ethylene and cyclopentene. The 1,2- and 1,3-insertion of cyclopentene into the polyethylene main chain was confirmed. This evidence strongly implies that Cr=C may not be the active site for chain propagation, and indicates that the Cr-C active sites model under Cossee-Arman chain propagation mechanism may be responsible for chain propagation during the normal polymerization period. The metathesis sites (chromium-carbene Cr=C species), during the induction period mentioned in our previous work, might be transformed to Cr-C as polymerization active sites during the polymerization stage.

Moreover, some novel Phillips type catalysts bearing special organo-siloxane ligands were also successfully synthesized through ligand modification. These catalysts showed high ability to produce polyethylene with new microstructures. This finding represents a new way to improve the performance of Cr-based catalysts for producing new PE products.

In conclusion, homo- and co- polymerization of ethylene and cyclopentene were carried out using Phillips catalyst with Al-alkyl cocatalyst. The promotion effect of cyclopentene on ethylene polymerization activity and improvement of the resulting polymer properties indicates very good prospects for future industrial applications. This finding has also led to a breakthrough in the investigation of the nature of the active sites and the polymerization mechanism. The development of novel Phillips type catalyst with Al-alkyl cocatalyst contributes to wider application of Phillips catalyst to traditional processes for producing PE products with improved properties.