

Title	エチレン重合における新規均一系シルセスシロキサン担体型クロム触媒の設計と高効率活性化剤の検討
Author(s)	Zeng, Yanning
Citation	
Issue Date	2015-03
Type	Thesis or Dissertation
Text version	ETD
URL	<a href="http://hdl.handle.net/10119/12770">http://hdl.handle.net/10119/12770</a>
Rights	
Description	Supervisor: 寺野 稔, マテリアルサイエンス研究科, 博士

氏名	YANNING ZENG		
学位の種類	博士(マテリアルサイエンス)		
学位記番号	博材第 369 号		
学位授与年月日	平成 27 年 3 月 20 日		
論文題目	Design of novel homogeneous chromium-based catalyst system using silsequioxane support and high-efficiency activator for ethylene polymerization (エチレン重合における新規均一系シルセスシロキサン担体型クロム触媒の設計と高効率活性化剤の検討)		
論文審査委員	主査	寺野 稔	北陸先端科学技術大学院大学 教授
		山口 政之	同 教授
		海老谷 幸喜	同 教授
		谷池 俊明	同 准教授
		野村 琴広	首都大学東京 教授

## 論文の内容の要旨

Phillips ( $\text{CrO}_x/\text{SiO}_2$ ) catalyst for ethylene polymerization has been utilized in industrial for more than 6 decades. The irreplaceable unique features of the Phillips catalysts are both ultra-broad molecular weight distribution (MWD) and adequate amounts of short and long chain branches incorporated. Finer control of the polymer structure and improvement of polymerization performance with the Phillips ethylene polymerization system have been continuously required. However, the factors for the control of the unique characters have not been systematically understood in view of chemistry despite the immense studies for Phillips ethylene polymerization system. The objective of this dissertation mainly is to investigate the relationship between local structures of Cr species and polymerization properties for knowledge of precise design of the Phillips-type catalysts and design the high-efficiency activator. Comprehensive investigations by both design of catalyst and selection of activator were attempted in this work. The series of results can be summarized as follows.

A series of Phillips-type bimetallic catalysts were prepared according to a co-impregnation method and their ethylene polymerization performances were examined. It was found that for the bimetallic approach, early transition metal as the second component offers improvements both in the activity and branching ability. The maximum performance improvements over the conventional Phillips catalyst are plausibly around several tens%. Interestingly, the addition of second metal components should alter the nature and density of surface hydroxyl groups similarly to the calcination temperature. However, the influences of the second metal components are much smaller than those of the calcination temperature. This fact may hide some key parameter(s) toward immense improvements of the catalyst

performances.

Various types of aluminum alkyl activator were employed to explore the performance and branching ability of Phillips catalyst. Polymer yield was found to be dependent on type and concentration of aluminum alkyl, in which the larger alkyl group enhanced the polymerization performance as a result of deactivation suppression. The suppression of deactivation to extend the concentration operation window could be also achieved by using BHT-passivated aluminum alkyl. However, the reduced reactivity of aluminum alkyl concurrently decreased the power of activation, resulting in low polymer yield. Frequency of  $\geq$  hex branches formed from the incorporation of in-situ  $\alpha$ -olefin followed the polymer yield, while the methyl branch of PE produced in the presence of different activators and concentrations was found to be associated with the degree of deactivation. The catalyst design is important tool to tune the polymerization performance, whilst the design of activator system emerges comparable or much more role in tuning the polymerization performance and polymer properties.

At last, the homogeneous model catalysts with uniform structure prepared using POSS as support was studied to understand industrial Phillips catalyst. The homogeneous model catalysts without hydroxyl group in catalyst structure can produce polymer, it indicated the hydroxyl group is not necessary for Phillips ethylene polymerization. Meanwhile, they can make the polymer with very broad MWD, plausibly it originated from the reaction between catalyst and activator. The homogeneous model catalysts with different oxidation state showed a similar ethylene polymerization performance on polymer properties. A hexavalent catalyst imparted a higher activity is more stable than trivalent one during polymerization. Different local environment for chromium active site also imparted a various deactivation for broad MWD.

Thus obtained discussion in this work suggests for finer design of Phillips ethylene polymerization system to improve the Phillips ethylene polymerization performance and control the molecular weight, branches and their distribution in PE. The results and discussion in this dissertation will be helpful in improvement of the world wide used catalyst and in development for novel oxide based olefin polymerization catalyst system.

**Key word:** Phillips catalyst, Activator, Ethylene polymerization, Polyethylene, Silsequioxne.

## 論文審査の結果の要旨

Phillips catalysts composed of  $\text{CrO}_x$  supported on silica have long maintained their industrial significance in the polyolefin manufacture to produce nearly 10 million tons of a special grade of HDPE per year all over the world. The specialty of the Phillips catalysts is an ability to produce HDPE with fine mechanical properties such as elasticity and impact resistance, and superior moldability due to its high melt viscosity. These properties come from both broad molecular weight distribution (MWD) and

adequate amounts of short and long chain branches (SCBs and LCBs) incorporated. Although finer controls of polymer micro structures by the Phillips catalysts have been continuous demands for further multipurpose materials, significant efforts still deposit obscurities in the mechanistic origin of the unique catalytic features.

This dissertation is to investigate the relationship between local environments of chromium active site and oxidation states of chromium active site. The polymerization properties and the branching abilities for the precise design of the Phillips-type catalysts. For this purpose, comprehensive investigations including both catalyst and activator were attempted. The specific homogeneous model catalyst system having controlled local environments of chromium species and chromium active site structure was employed for ethylene polymerization. The investigation of local environments of chromium species using the homogeneous catalysts on the origin of unique structures of produced PE by Phillips catalysts has never been undertaken so far. Meanwhile, investigation of bimetallic chromium based catalyst and various activators for ethylene polymerization system were performed to improve polymerization behaviors and control the obtained polymer structure. It was found that novel homogenous analog of Phillips catalyst with uniform chromium oxidation state and controlled local environment fabricated polymer with broad MWD, indicating that broad MWD by Phillips ethylene polymerization originated from activation and deactivation during polymerization. The polymerization performance and branching ability of chromium based catalyst can be enhanced by modification by second metal with low electronegativity and the suppression of deactivation by appropriate activator.

The obtained results in this doctoral dissertation indicated the direction for the finer design of chromium based catalysts to control a MW, branches and their distribution in PE. The results and discussion in this dissertation will be helpful in improvement of the world wide used catalyst and in development for novel oxide based olefin polymerization catalysts.

As mentioned above, this dissertation greatly contributes to the understanding of the specific features of one of the most important industrial catalysts for ethylene polymerization. Therefore, this dissertation can be recommended for the doctor degree of JAIST in the field of materials science.