Title	分子触媒と固体触媒の概念を融合したオレフィン重合触媒の開発
Author(s)	馬場，竜希
Citation	
Issue Date	2019-03
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/15799
Rights	
Description	Supervisor:谷池　俊明，先端科学技術研究科，博士

Development of Olefin Polymerization Catalysts by Bridging Molecular and Solid Catalyst Concepts

Taniike Laboratory, Student Number: 1620020, Ryuki Baba

Solid catalysts and molecular catalysts have been developed in the field of olefin polymerization catalysts. In the solid catalyst, it is difficult to clarify the structure-performance relationship (SPR) and reaction mechanism because various chemical and physical structural factors ranging from atoms to the particle size scale exist and its performance emerges as a sum of a large number of catalytic active sites. Evaluation of the nature of well-defined active sites by the surface organometallic chemistry (SOMC) approach has advanced, but complete understanding is not easy. On the other hand, the molecular catalyst is powerful not only to understand the reaction mechanism but also to design the catalyst function since a single structure endows a clear relationship with the produced polymer structure. However, catalytic multifunctionalization by multinuclear complexation or loading on a solid support is required to obtain a unique polymer structure and there are problems such as restriction on synthesis of ligands and unevenness of active site structure. Molecular catalysts that mimic traced chemical structure of solid catalyst or precise enable function accumulation in a single molecule are strongly required to fill the gap between the solid and molecular catalysts. In this dissertation, the purpose is to establish catalyst combining the concepts of solid and molecular catalyst through the study of molecular catalyst that mimics solid catalyst structure with a systematic design and polymer-supported catalyst possessing well defined active site structures and multifunctionality.

In Chapter 2, polyhedral oligomeric silsesquioxanes (POSS) supported Phillips-type molecular catalysts for ethylene polymerization were synthesized to minimize the heterogeneity of solid support surfaces. A series of POSS-supported chromium catalysts with different active-site environments were obtained by the introduction of different functional groups. Their ethylene polymerization performances were influenced by the functional groups. Especially, diphenylphosphino group improved the activity and provided a bimodal polyethylene (PE). The similar result was confirmed in diphenylphosphino group modified silica supported catalyst. It was revealed that the design strategy based on the support functionalization can be transferred to SiO_2-supported chromium catalysts.

In Chapter 3, a series of POSS-supported chromium catalyst was used with various alkyl aluminum ($AlEt_3$, Al^iBu_3, Al^nOt_3) and $Ph_3CB(C_6F_5)_4$ to reveal the influences on the catalyst performance. The activity of POSS-supported chromium catalyst with alkylaluminum was determined by the balance of activation and deactivation. In contrary, $Al^iBu_3/Ph_3CB(C_6F_5)_4$ system constantly enhance the activity since it stabilized the chromium site as cationic species. In particular, the catalyst having diphenylphosphino group was improved the activity and influenced the molecular weight distribution. The co-catalyst system also enhanced the ethylene/1-octene copolymerization activity. It was revealed that the choice of functional group and activator is crucial for determination the catalyst performance.

In Chapter 4, a new type olefin polymerization catalyst which can accumulate multiple active sites with clear structure on one polymer chain was investigated to bridge the gap between solid and molecular catalyst. A series of polynorbornene (PNB)-support possessing different functional groups were synthesized by ring-opening metathesis polymerization using Grubbs catalyst. Copolymers and terpolymer possessing aryloxo group and/or phenoxyimine group were synthesized. The structure of PNB-supports were controlled precisely and Cp^*TiMe_3 were grafted on them successfully. The terPNB-supported catalyst exhibited higher activity compared with a mixture of each PNB-supported catalyst having sole active site species. Polyethylene produced by the terPNB-supported catalyst showed good elongation property compared with tandem molecular/PNB-supported catalyst systems. It indicated that ternary PNB-supported catalyst produced uniformly dispersed PE which generating from different active sites. It was found that PNB-supported catalyst has a unique catalyst features and is promising for develop a novel catalyst class.

Thus, these results in this work suggests a series of model molecular catalysts with systematic design is a useful tool for the better understanding of a solid catalyst performance and the bridging of multiple active site on polymer chains shows unique catalyst performance. The results in this dissertation can be applied to other catalyst systems and will contribute developments of catalyst chemistry.

Key word: olefin polymerization, bridging catalyst, Phillips catalyst, silsesquioxane, soluble polymer support