

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
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論文題目	Development of Olefin Polymerization Catalysts by Bridging Molecular and Solid Catalyst Concepts		
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論文の内容の要旨

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 SiO₂-supported chromium catalysts.

In Chapter 3, a series of POSS-supported chromium catalyst was used with various alkyl aluminum (AlEt₃, AlⁱBu₃, AlⁿOt₃) and Ph₃CB(C₆F₅)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, AlⁱBu₃/Ph₃CB(C₆F₅)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*TiMe₃ 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

論文審査の結果の要旨

全化学プロセスの約 70%に寄与する触媒材料は、固体表面の配位不飽和性を利用した固体触媒と酸や有機金属錯体等を含む分子触媒という 2 つの概念に大分される。固体触媒は、安価・高温安定性・易分離性といった長所に加えて、役割の異なる触媒成分をマルチスケールに渡って設計された形態の中に集積させることができるため、概して多機能的である。しかし、構造的な複雑さが故に、固体触媒は得てして不均一であり、系統的な設計や活性・選択性の点で分子触媒に劣る。一方、分子触媒は構造が分子レベルで均一であるが故に、設計性・活性・選択性に優れるが、同時に単機能的でもある。従って、固体触媒と分子触媒の各々の長所を併せ持つ概念融合型触媒は、当該分野における重要課題として認識されてきた。

本論文では、幾つかの概念融合型触媒を新規に合成し、触媒多機能性を分子レベル設計の中で実現することに成功した。高密度ポリエチレンの製造を担う Phillips 触媒に関して、 SiO_2 表面上の水酸基の分布に端を発する不均一性が活性中心たる Cr 種の構造設計や機構解明における長年の妨げとなっていた。本研究では、不完全縮合ポリヘドラルオリゴシルセスキオキサン (POSS) を用いた種々の新規 Phillips 型分子触媒を開発し、Cr 活性中心近傍のヘミレーバイル配位基によって活性の向上や分子量分布の拡大が可能であるという新しい設計軸を見出した。また、この設計が実際の固体触媒の改良においても有効であることを実証した。さらに、開発した分子触媒を *in-situ* 分光分析 (紫外可視吸光分光、NMR) と組み合わせることで、活性種の正体やその失活機構を分子レベルで解明することにも成功した。このような分子レベルの設計や機構解明は、本研究で開発した分子触媒無しには実現し得なかったものである。ヘミレーバイル配位基は Cr 中心に可逆的に配位することで失活を抑制し、活性化剤である有機アルミニウムに可逆的に配位することで第二の活性種を与える。

他にも、ランダムコイル状のポリノルボルネン鎖に性能の異なる 2 種のハーフチタノセン錯体を集積した、2 核型高分子鎖担持触媒を初めて合成することに成功した。開発した触媒は、非担持の分子触媒に匹敵するエチレン重合活性を示し、特に、2 種の分子触媒を単純に混合し得られたポリエチレンと比較して、2 核型高分子鎖担持触媒を用いて得られたポリエチレンは分子レベルで混合されており、韌性に優れていた。

以上、本論文は、分子触媒と固体触媒の特長を併せ持つ概念融合型触媒に関して、新規触媒の開発とこれらを用いた触媒機能の改良や解明に成功し、触媒分野に非常に重要な進展をもたらした。よって、博士 (マテリアルサイエンス) の学位論文として十分価値あるものと認めた。