

Title	マルチグレイン構造を有するモデルZiegler-Natta触媒を利用した構造性能相関の解明
Author(s)	池田, 智博
Citation	
Issue Date	2022-03
Type	Thesis or Dissertation
Text version	ETD
URL	<a href="http://hdl.handle.net/10119/17775">http://hdl.handle.net/10119/17775</a>
Rights	
Description	Supervisor:谷池 俊明, 先端科学技術研究科, 博士

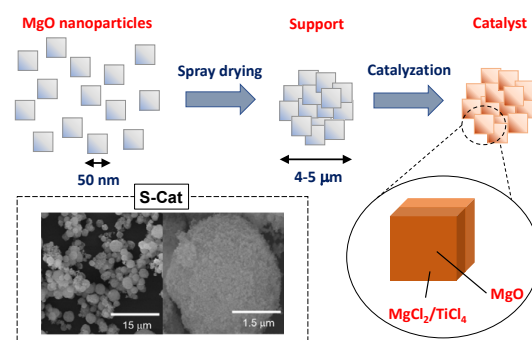
氏名	池田智博		
学位の種類	博士(マテリアルサイエンス)		
学位記番号	博材第537号		
学位授与年月日	令和4年3月24日		
論文題目	Fabrication of model multi-grain structures in Ziegler-Natta catalyst for investigation of structure-performance relationship		
論文審査委員	主査	谷池俊明	北陸先端科学技術大学院大学 教授
		桶葎興資	同 准教授
		篠原健一	同 准教授
		都英次郎	同 准教授
		塩野毅	広島大学 教授

## 論文の内容の要旨

Heterogeneous Ziegler-Natta catalysts (ZNC) is one of the most popular catalysts in the polyolefin production. The catalyst particle has a specific interior structure called multi-grain structure, where nanometer-order basic constituent units (catalyst primary particles) aggregate. This porous structure is thought to be closely related to catalytic performance through the diffusion of monomers and co-catalysts. However, it has been difficult to independently control several structural parameters such as primary particle size and pore volume in top-down preparation methods such as chemical method, which is currently the mainstream method where support formation and catalysis proceed simultaneously. In this study, I propose a new catalyst preparation method in which MgO nanoparticles are formed into spherical aggregates by spray-drying and then treated with  $\text{TiCl}_4$ . By using MgO nanoparticles as the primary catalyst particles, the morphology of the macro-particles can be created in a bottom-up manner. With this model catalyst having multi-grain structures, the structure-performance relationship of ZNC was investigated. Moreover, the model catalyst was applied to the synthesis of micro-fine grade ultra-high molecular weight polyethylene (UHMWPE) and isotactic polypropylene.

In chapter 1, MgO nanoparticles with a particle size of 50 nm were agglomerated using a spray dryer to prepare spherical supports. After optimizing the conditions, spherical supports were obtained stably at a spray temperature of 160 °C, a slurry feed rate of 800 ml  $\text{h}^{-1}$ , a spray pressure of 200 kPa, and a slurry concentration of 4 g  $\text{L}^{-1}$ . The secondary particle model catalyst (S-Cat) was prepared by treating the support with  $\text{TiCl}_4$  (Figure 1). The catalyst macro-particles were spherical in shape with a size of about 5  $\mu\text{m}$  and a narrow particle size distribution (RSF = 0.3). As a comparison of S-Cat, a primary particle model catalyst (PA-Cat50) was prepared by modifying magnesium oxide nanoparticles with surfactants and then catalyzed with  $\text{TiCl}_4$ . The PA-Cat50 and S-Cat catalysts exhibited decay kinetics with high initial activity and rapid deactivation in both ethylene and propylene polymerization. It has been experimentally demonstrated that the pores whose diameter is over 2 nm do not restrict the mass diffusion.

In chapter 2, S-Cat was used to synthesize micro-fine grade UHMWPE with a particle size of several tens of micrometer. In order to change the macro-particle size and the pore volume of the support, the concentration of MgO slurry fed to the spray drying process was varied. With the obtained catalyst samples, ethylene polymerization was carried out at a temperature of 70 °C, a pressure of 0.8



**Figure 1.** Synthesis route and SEM image of

MPa, and a polymerization time of 2 h. There was no correlation between structure and activity among the catalyst samples, and the activity was about 30-45 t-PE mol-Ti<sup>-1</sup> h<sup>-1</sup>. The resulting PE particles were sphere with a particle size of about 50 μm and had a molecular weight of about 4.0×10<sup>6</sup> g mol<sup>-1</sup>. When films were prepared by compression molding using each polymer sample, fusion started at a lower temperature than PE synthesized with a normal grade industrial catalyst (Ind. Cat), and melting was confirmed at 120°C, similar to PE synthesized with PS-Cat50. However, there was no difference in melting point and crystallization temperature among the PE samples synthesized by S-Cat, PA-Cat50, and Ind. Cat.

DBP doped S-Cat were prepared for the synthesis of isotactic polypropylene. The Ti/DBP ratio was varied according to the number of TiCl<sub>4</sub> treatments during the catalyst preparation. The DBP content was about 3 % for the catalyst with one treatment (S-Cat B) and about 1 % for the catalyst with two treatments (S-CatC). The primary and secondary particles of the supports did not fuse or deform and maintained their morphology after DBP addition. As a result of propylene polymerization, the activity of S-CatB and S-CatC was lower than that of the donor-free catalyst (S-CatA), but the PP consisting of 90% mesopentad was obtained, which is about 10% higher than that of S-CatA.

In this study, new model ZNCs with multi-grain structure were successfully prepared by spray-drying MgO nanoparticles for the first time by a bottom-up method. Compared with existing preparation methods, the catalyst structure can be changed intentionally, and the catalyst can be further developed to study the structure-performance relationship and to synthesize polymers of the desired standard.

Key word: Ziegler-Natta catalyst, bottom-up synthesis, structure-performance relationship, UHMWPE, isotactic polypropylene

## 論文審査の結果の要旨

本論文は、酸化マグネシウム (MgO) 単結晶ナノ粒子の凝集制御を基盤とした、マルチグレイン構造を有する Ziegler-Natta オレフィン重合触媒の調製とこれを用いた構造性能相関研究に関する成果をまとめたものである。

ポリオレフィン製造の主軸を担う不均一系 Ziegler-Natta 触媒は、触媒成分が共担持された塩化マグネシウム (MgCl<sub>2</sub>) のナノ構造体を基本単位とし、これが不規則かつ階層的に凝集することで多孔質な亜球状マクロ粒子を形成している。このような粒子構造はマルチグレイン構造と呼ばれ、粒子内細孔への基質拡散、重合に伴う粒子の段階的なフラグメンテーションを通して、生成するポリマー粒子の形態や滞留中の活性挙動の制御において必要不可欠とされてきた。しかし、不規則なマルチグレイン構造をトップダウン的な触媒調製の過程で制御し定量することは著しく困難であり、これが系統的な触媒開発のための構造性能相関解明の大きなボトルネックとなっていた。

本論文では、MgO 粉末を塩化チタン (TiCl<sub>4</sub>) 処理によって触媒化するプロセスに着目し、サイズ制御された MgO 単結晶ナノ粒子をスプレードライ法で二次凝集させた後に触媒化することで、マルチグレイン構造と均一な粒子径を有する Ziegler-Natta 触媒のボトムアップ的な調製に成功した。この際、スラリー濃度や MgO ナノ粒子のサイズを通じて、マクロ粒子径や細孔容積などをある程度制御できることも見出した。50 nm 大の MgO 単結晶ナノ粒子を用いた際、二次粒子触媒は一次粒子触媒と同様な活性挙動を示し、メソ孔が基質拡散に影響しないことを明らかにした。二次粒子触媒は球状のハンドリング性に優れたポリマー粉末を与えた。このような結果を受け、第三章では二次粒子触媒を超高分子量ポリエチレンの合成に応用し、塩素残渣が少なく、ポリマー粉末の圧縮成形において顕著な低温融着性を示す超高分子量ポリエチレン粉末を得た。第四章では、触媒化の際にドナーを共担持する調製法を開

発し、モデル的なマルチグレイン構造を有するだけでなく、プロピレン重合において実用的な活性と立体特異性を示す触媒を調製することに成功した。

以上、本論文では、モデル的なマルチグレイン構造を有する **Ziegler-Natta** 触媒系を開発し、これを用いて構造性能相関やポリマーの形態制御に関する有用な知見を導くことに成功しており、当該分野の進展への貢献は大きい。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。