

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
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Fabrication of model multi-grain structures in Ziegler-Natta catalyst for investigation of structure-performance relationship

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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 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 h⁻¹, a spray pressure of 200 kPa, and a slurry concentration of 4 g L⁻¹. The secondary particle model catalyst (S-Cat) was prepared by treating the support with TiCl_4 (Figure 1). The catalyst macro-particles were spherical in shape with a size of about 5 μm 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 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 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⁻¹ Ti⁻¹ h⁻¹. The resulting PE particles were sphere with a particle size of about 50 μm and had a molecular weight of about 4.0×10⁶ g mol⁻¹. 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_4 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.

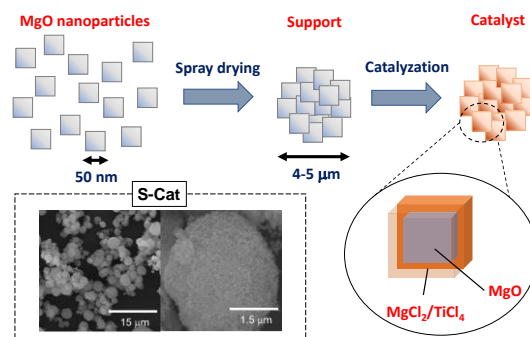


Figure 1. Synthesis route and SEM image of S-Cat.

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