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Effects of Catalyst Particle Structure on Catalytic Properties in Heterogeneous Ziegler-Natta Olefin Polymerization

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1. Background

Polyolefins (POs), which include homo-, or co-polymers of α -olefins such as polyethylene (PE), polypropylene (PP), are the most popular plastics over the world. PO production is mainly based on catalytic polymerization processes at a relatively low monomer pressure. Ziegler-Natta (ZN) catalyst is the most important class among PO production catalysts, as being responsible for more than half of high-density and linear low-density PE, and especially for most of PP. In ZN olefin polymerization, the catalyst particle structure has been found to play vital roles in production process. For example, physical characteristics of the original catalyst like shape, particle size distribution, bulk density, etc., determines those of the final polymer particles, which has strong influences on polymer production and processing, through a growing process named replication phenomena [1]. The catalyst particle architecture affects to the copolymerization efficiency as well as the distribution of different components in one polymer particle, in consequence have large impact on properties of the polymer alloy [2]. In another example, the catalysts with different pore systems show very different kinetic profiles in ethylene polymerization [3]. Because of its significance, a great number of researches about the effects of the catalyst particle structure on the catalytic properties in olefin polymerizations have been performed. The mechanisms of those phenomena, however, are still far from a full understanding, leading to difficulties in further exploiting advantages of the catalyst particle structure on PO production and properties.

2. Objective

This dissertation studies on the effects of the catalyst particle structure on catalytic properties in olefin polymerization, aiming at elucidation of the mechanisms behind those functions. In order to fulfill this target, a number of catalyst systems, whose structure was carefully characterized by combination of various methods, and different polymerization techniques have been utilized. The results obtained in this work are expected to contribute to a total understanding about the roles of catalyst particle structure, which is essential for development of new generation heterogeneous catalyst systems.

3. Results and Discussion

3.1 Effects of catalyst particle architecture on initial particle morphology development

It has been known that the morphology of polymer particles is mainly determined by that of the original catalyst particles as well as the way of the particles growth, especially at the initial stage of polymerization due to the friability of polymer/catalyst particles at this stage. However, study about the initial particle growth suffers difficulties in the very short time scale of this stage. In this study, stopped-flow (SF) polymerization technique, which was originally applied to investigate the very early kinetics in heterogeneous olefin polymerization, has been employed to continuously capture the particle growth. The catalyst in this study was prepared by the chemical reaction method, so-called Cat-C, which is widely used for industrial production of homo and high-impact PP.

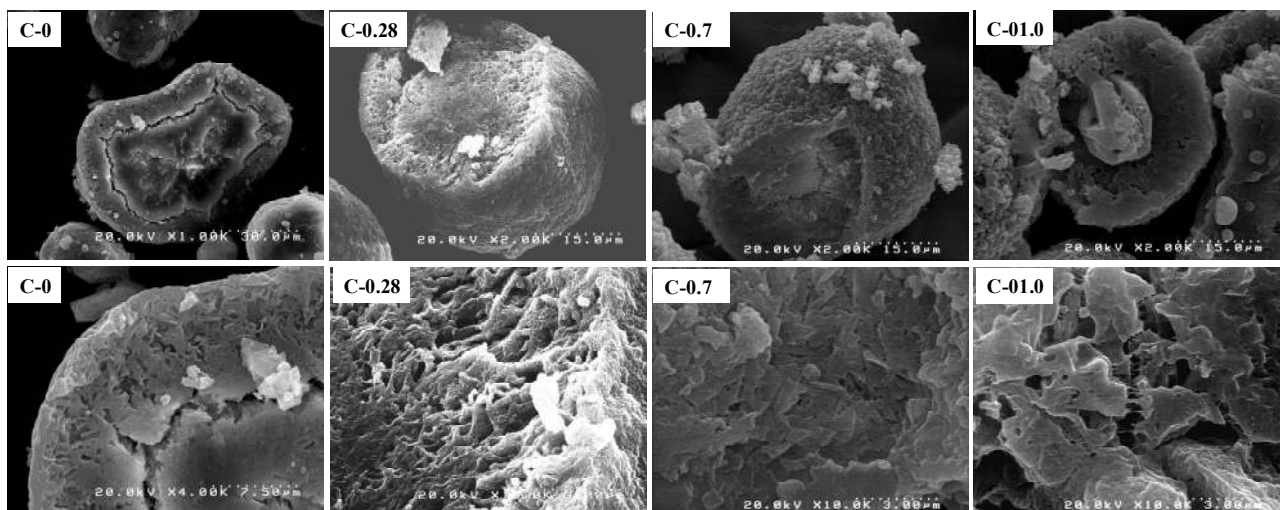


Fig. 1 Cross-sectioned SEM images of catalyst and polymer/catalyst particles, the number in label indicates the polymer yield (g-polymer/g-catalyst) of samples.

Scanning electron microscope (SEM) images in Figure 1 show the initial bulk morphology development in propylene polymerization. The original catalyst particle has a layered architecture consisting of three parts: a thin and dense shell at the outermost part, a porous layer at the middle, and a compact core at the center. The porous layer and the compact core are made from randomly or orderly stacked lamellae, respectively. Fig. 1 C-0.27 demonstrates the shrinkage of macropores in the middle layer, indicating that they were partially filled by the formed polymer. At the polymer yield of 0.7 g-polymer/g-catalyst, the macropores in the middle layer was hardly observed. It means this layer was mostly filled by produced PP. In the magnified image C-0.7, the appearance of polymer fibrils among lamellae pointed out that the lamellae start to separate from each other. When the polymerization proceeded, the further expansion of the middle layer created new macropores (C-1.0). The fragmentation of the middle layer induced the fragmentation of the outermost shell and the core at the later stage. Therefore, the effects of the catalyst particle architecture on the morphology control is concluded that a small amount of polymer mildly produced in the outermost shell and middle layer significantly strengthened the particles, preventing them from the severe disintegration often occurs at the initial stage.

3.2 Effects of catalyst particle structure on olefin polymerization kinetics

Previous studies have shown big influences of pore system in catalyst particle on the polymerization kinetics, however, there is no clarification about the roles of each class of pores as well as their spatial distribution. The second part of the dissertation was devoted to elucidate this problem. Ethylene or propylene homopolymerization kinetics was measured with three catalysts, which were prepared by chemical, solution, and grinding methods, namely Cat-C, Cat-S, and Cat-G, respectively. In order to eliminate the effects of variation in active site nature and polymerization conditions on kinetics, three catalysts were synthesized with the same chemical composition, and polymerizations were conducted in completely similar conditions. The pores, pore size distribution, and spatial distribution of pore were carefully determined by combination of N_2 adsorption/desorption measurement, mercury porosimetry, and cross-sectioned SEM.

Propylene polymerization kinetics of all three catalysts is of decay-type with a fast activation and long deactivation period. However, the time required to get the highest rate change in order $Cat-G < Cat-C < Cat-S$, in line with the number of macropore decreases from Cat-G, Cat-C, to Cat-S, indicating that the catalyst with larger pore volume is fragmented more easily than the dense catalyst. In another aspect, the stability of polymerization rate

(indicated by ratio of the rate after 1 h to the highest rate) increases from Cat-G, Cat-C, to Cat-S, being in a similar trend with the number of micropore in these catalysts. The fact can be explained by the potential active sites located in micropore are gradually exposed to monomer as a consequence of fragmentation during polymerization, therefore the larger number of micropores, the more stable the polymerization rate. In ethylene polymerization, while the Cat-C and Cat-G still show the decay-type kinetic profiles, the Cat-S shows a build-up type profile with step-wise activation. Because of the high crystallinity of the produced PE and compactness of the Cat-S, the monomer diffusion to inner part of catalyst particle is restricted. The polymerization rate is accelerated when the outer layer is fragmented to make new access for monomer to the inner active sites. This type of layer-by-layer fragmentation mode results in a step-wise activation and a cobweb polymer morphology.

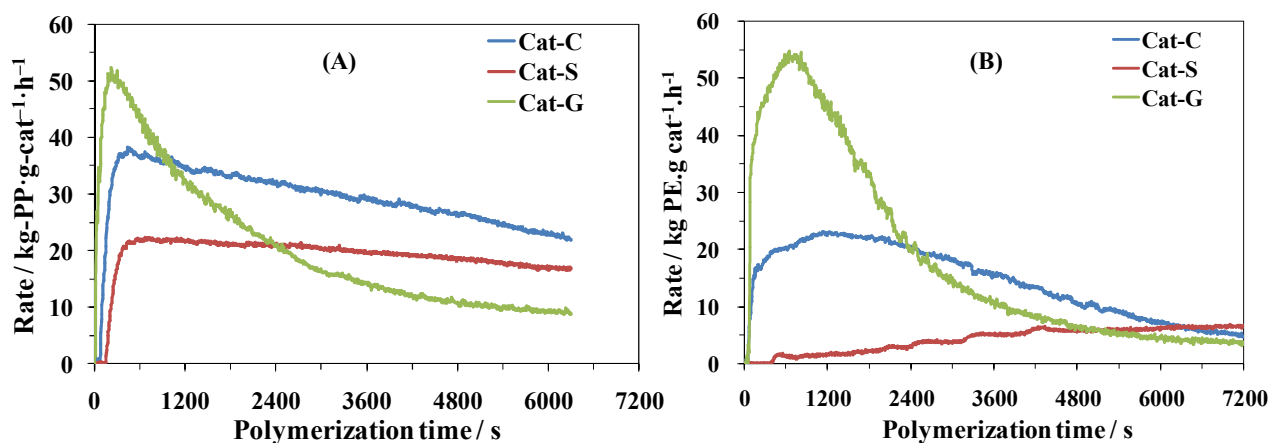


Fig. 2 Propylene (A), or ethylene (B) polymerization kinetics with Cat-C (blue), Cat-S (red), and Cat-G (green)

3.3 Activity-surface area relationship in propylene polymerization with novel core-shell MgO/MgCl₂/TiCl₄ catalysts

The catalyst specific surface area and its activity in MgCl₂-supported ZN olefin polymerization have a very poor correlation owing to the shape irregularity and the size distribution of pores. Therefore, in order to obtain the activity-surface area relationship, the simplification of the catalyst structure is necessary. In this part, this relationship has been established for the first time on the basis of novel core-shell MgO/MgCl₂/TiCl₄ catalysts. Starting from single-crystal MgO nanoparticles with various particle sizes and specific surface areas, a series of core-shell MgO/MgCl₂/TiCl₄ catalysts were fabricated, in which the poreless and non-fragmentable MgO core was covered by a thin layer of the catalytic components. While these catalysts exhibited active site natures typical for MgCl₂-supported ZN catalysts in propylene polymerization, the poreless and non-fragmentable features gave a perfectly proportional relation between the catalyst activity and its specific surface area as shown in Fig. 3.

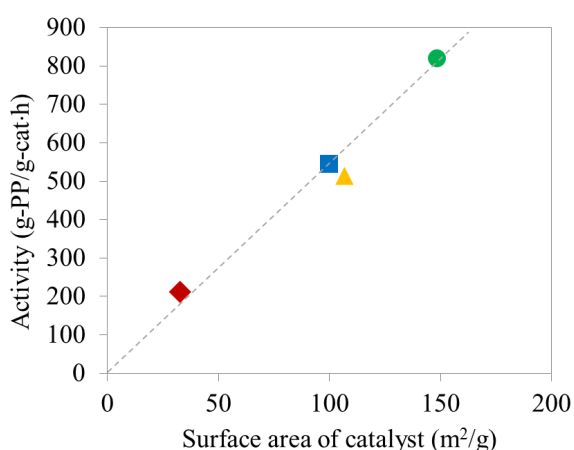


Fig. 3 Dependence of catalyst activity on specific surface area in propylene polymerization with MgCl₂-supported ZN catalyst

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Achievements

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