The Synthesis of Isotactic Polypropylene with Spherical Morphology via Supported Metallocene Catalyst

Han HONG, Wei Dong YAN, Ming Ge ZHANG, Nai ZHOU, Da Wei HE, You Liang HU**

State Key Lab of Engineering Plastics, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: Polymerization of propylene was carried out under bulk process at 70°C using the supported metallocene catalyst with four kinds of SiO_2 as carrier with triethylaluminum used as co-catalyst. The morphology of the products was studied by SEM. It was found the property of the carriers gave great effect on the fine structure of the products as well as the appearance.

Keywords: Isotactic Polypropylene, spherical morphology, supported metallocene catalyst.

The morphology control of polypropylene products is one of the technological obstacles to the industrial polymerization of propylene *via* metallocene catalyst. One efficient way to solve this problem had been proposed that the metallocene catalyst should be supported on suitable carrier. Although lots of work has been reported¹⁻³, up to date, no breakthrough has been got yet. The studies on morphology control of supported metallocene catalysts will be of great value in either scientific or practice view. In this paper we will report the morphology control results of the iPP attained under the commercial polymerization conditions (bulk process, Tp=70°C) *via* the supported metallocene catalyst SiO₂/MAO/*rac*-Me₂Si[2-Me-4-Naph-Ind]₂ZrCl₂.

The method for making the supported metallocene catalyst is of high efficiency (in preparation to be published). Here we made four kinds of the supported metallocene catalyst $SiO_2/MAO/rac$ -Me₂Si[2-Me-4-Naph-Ind]₂ZrCl₂ with different carriers: regarded as SiO_22407 #; SiO_22408 #; SiO_23030 #; SiO_23050 #. SiO_22407 # and SiO_22408 # were purchased from Grace Davison Corporation with the product number XPO-2407 and XPO-2408 respectively. While SiO_23030 # and SiO_23050 # were purchased from PQ Corporation with the product number MS-3030 and MS-3050 respectively. The polymerization was carried out in 3-litter autoclave at 70°C for 1 hour. Triethylaluminum was used as co-catalyst. The morphology of the product was detected by Hitach-500 scanning electron microscope.

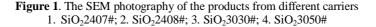
The alkylaluminum can not be used as co-catalyst for the homogeneous metallocene catalyst. But we found that for the supported metallocene catalyst

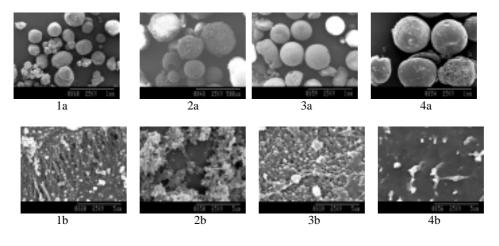
SiO₂/MAO/*rac*-Me₂Si[2-Me-4-Naph-Ind]₂ZrCl₂, several kinds of alkylaluminum could be used as co-catalyst to give good polymerization results. In our study, when triethylaluminum was used as co-catalyst, the morphology of the attainted polypropylene

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was spherical for all samples as shown in **Figure 1** ($1a \sim 4a$). But the appearance of the particles strongly depended upon the properties of the carrier SiO₂ that the supported catalyst used. When SiO₂2407# (1a) and SiO₂2408# (2a) were used as the carrier, the surface of the product was very rough and coarse; while SiO₂3030# (3a) and SiO₂3050# (4a) were used as carrier, the surface of the product was rather smooth and round.

The fine structure of the surface of the products (1b~4b) illustrated the difference more clearly. When SiO₂2407# was used as the carrier, the surface (1b) of the product was not uniform but continuous. There are lots of fibers between the bulk matrix. When SiO₂2408# was used as the carrier, the surface (2b) of the product was not continuous and there is large hole among the cluster-like matrix. When SiO₂3030# was used as carrier, the surface (3b) of the product was rough uniform continuous phase with lots of pores. When SiO₂3050# was used as carrier, the surface (4b) of the product was smooth uniform continuous phase. The great dissimilarity of the product morphology may be due to the difference of the carriers in their particle size, surface area, pore value, and pore size distribution. The study of mechanism of effect of the carrier's properties on the morphology is undergoing.





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