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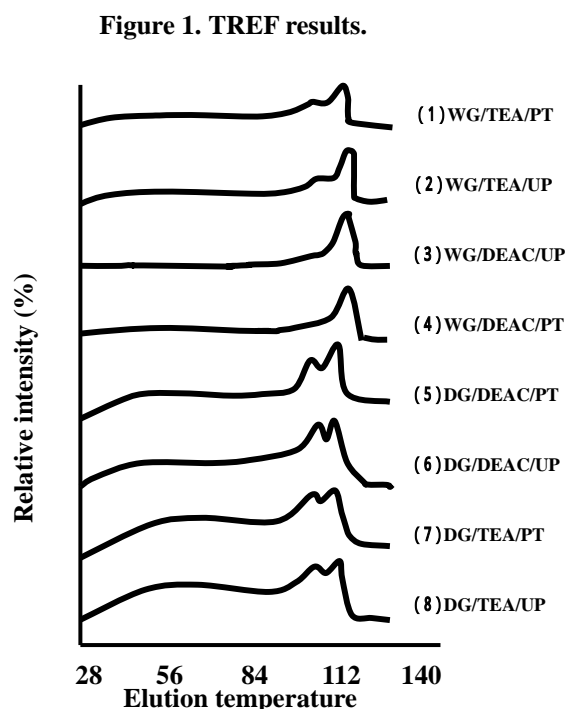
C17p5 Origin of Isospecificity of Donor-Free TiCl_3 -Based Ziegler-Natta Catalysts for Propylene Polymerization

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【Introduction】 Ziegler-Natta catalysts, after the discovery in the early 1950s, are still extensively applied for the large-scale production of polypropylene (PP). A great number of research efforts have been devoted to improve the catalytic activity and stereospecificity. Even after 50 years of development, many details of the reactions leading to the isospecific active sites still remain unclarified. With the simplest components, the original type of TiCl_3 -based heterogeneous catalyst having its ability to produce highly isotactic polypropylene fractions without using electron donors, can be an ideal model for the study on the origin of isospecificity of active sites. The aim of the present study is to get better understanding concerning the origin of isospecificity of TiCl_3 -based Ziegler-Natta catalysts.

【Experiments】 Experiments include the preparation of MgCl_2 -supported and unsupported AA- TiCl_3 catalyst by wet ground (WG) and dry ground (DG) methods, slurry propylene polymerization, and characterization of catalysts and PPs by various techniques. Propylene polymerization was conducted applying pretreatment (PT) or unpretreatment (UP) of catalysts with triethylaluminum (TEA) or diethylaluminumchloride (DEAC) as a cocatalyst. The analyses involve estimation of isotacticity in terms of mesopentad fractions by ^{13}C -NMR and state of isospecificity with respect to isotacticity distribution of PPs by TREF techniques.

【Results and discussion】 Particle size distribution measurement showed finer particle size with good morphology for WG catalyst, which has higher activity in comparison to DG catalyst. TREF analysis shows different isospecific active sites distribution according to crystallinity of PPs produced with DG catalyst in comparison to WG catalyst as shown in Fig. 1. Pretreatment does not change the distribution of isospecificity of active sites. As a cocatalyst, TEA provided more efficiency than DEAC to get higher activity and isospecificity with both WG and DG catalysts. This might be rationalized by the fact that TEA has higher alkylating ability than that of DEAC. The variations of isospecificity of active sites occur due to the presence of MgCl_2 -support and different grinding methods. During grinding, TiCl_3 catalyst particles are dispersed randomly on the MgCl_2 surface. Solvent in WG method may prevent the change of originally-arranged active species by providing layer wise fragmentation of primary catalyst particle. Based on these results, better understanding concerning the origin of isospecificity of donor-free TiCl_3 -based catalysts has been obtained.



Keywords

Isospecificity, Heterogeneous Ziegler-Natta catalyst, PP, mesopentad fraction, propylene polymerization.