Surface characterization of olefin polymerization catalysts by high spatial resolution analytical methods

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Abstract

Despite the great progress of the performance of Ziegler-Natta catalysts for olefin polymerization, many important questions concerning both the reaction mechanism and the structure of the active sites remain far from being clarified. The elucidation of these problems inevitably demands the application of surface analytical methods, which are potentially capable of providing information on the molecular level reaction.

Since the early 1970s, the progress of surface science has made significant contributions to the understanding of catalyst-based chemical and petroleum technologies. Modern surface science is known to provide insights into catalytic reaction occurred on the surface of heterogeneous catalyst.

High resolution transmission electron microscopy (HRTEM) has been regarded as a powerful tool which can provide direct images of a projected structure. Unfortunately, the investigations using HRTEM were limited to the materials insensitive to air or water, such as metal particles, oxide surfaces. Objective of this study, surface characterization of Ziegler-Natta catalyst used high spatial resolution analytical methods as the HRTEM.

Ziegler-Natta catalyst is known to be very sensitive to moisture and oxygen in the atmosphere. The reactions of the catalyst with these impurities proceed resulting in the loss of the activity for olefin polymerization. The structure of active sites in the catalyst seems to change quickly by these deactivation reactions. In this study, all samples are treated strictly under nitrogen in a glove bag to prevent the samples from the interaction with moisture and oxygen.

Pure $TiCl_3$ and $MgCl_2$ were observed by HRTEM. Existence of the lattice fringes was confirmed in the outermost surface of the $TiCl_3$ and $MgCl_2$. It becomes clear that the HRTEM can provide the unique information through the direct observation of the crystalline structure of the Ziegler-Natta catalyst.

For atomic level observation by HRTEM which needs crystallinity of the sample, model $MgCl_2$-supported Ziegler catalysts were prepared by vapor deposition method. The catalysts has the polymerization activity was checked from existence of polymer on the catalyst after exposed to the cocatalyst and propene by Time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis. The changes of the catalyst surface structure on each stage in catalyst preparation was observed by HRTEM.

Industrial $TiCl_3$ catalyst and several types of $MgCl_2$-supported Ziegler catalyst were observed by HRTEM. The distinguishable differences of the surface features and the distribution of the crystalline regions, that is the crystalline-amorphous structures, are directly observed by HRTEM. The catalyst preparation methods and kinds of raw materials are

found to affect the variation in the distribution of the crystalline regions in the near-surface and interior regions, the difference of which are explicitly confirmed through the HRTEM analyses. In particular, the significant difference in the crystalline-amorphous structure between the catalysts obtained by the mechanical ground plus chemical process method and the only chemical process method is found in this study. These findings enable us to elucidate the relationship between the catalyst preparation procedure and the polymerization behavior.

In this dissertation, it is succeeded to the HRTEM observation of the Ziegler-Natta catalysts. Difference crystalline features of the various Ziegler-Natta catalysts were observed. From the results obtained by these approaches, it can be said that will lead to observation of active site in the future. Also the novel experimental technique of this dissertation described would be applicable to study the various types of ultra-high moisture sensitivity samples like Ziegler-Natta catalysts.