Abstract

The present dissertation describes analysis of titanium species on Ziegler-Natta catalysts which are industrially used to produce polyolefins. The purpose of this study is to clear the existing states of the titanium species using various physical analytical methods and polymerization kinetics.

To analyze the oxidative states of titanium species on Ziegler-Natta catalyst surface, various types of the catalysts were analyzed by using X-ray photoelectron spectroscopy (XPS). The binding energy of Ti $2p_{3/2}$ peak was found to be higher for a $MgCl_2$-supported catalyst than that for $TiCl_3$ due to the difference of the oxidative state of titanium species in both samples. The binding energy of Ti $2p_{3/2}$ peak shifted to the lower binding energy side by the reaction with a co-catalyst, and it decreased with the reaction time, indicating the proceeding of the reduction of titanium species. XPS was also employed to analyze the effect of an internal donor to the titanium species. It was suggested that the internal donor existed free from the titanium species on the catalysts.

The catalysts were analyzed by using scanning Auger electron microscopy (SAM) to analyze the dispersion of titanium species on the surface directly. The result suggested the difference between the surface distribution of titanium on the $TiCl_3$ and that on a $MgCl_2$-supported catalyst. Also, it was confirmed that preparation method of the catalysts had a great influence upon the distribution of the titanium species. These results demonstrated that SAM had great potential as an effective tool for the characterization of the catalysts.

Crystal lattices of $TiCl_3$ and $MgCl_2$ were successfully observed by high resolution transmission electron microscopy for primary investigation of direct observation of active sites of the Ziegler-Natta catalyst. It was observed that the crystal surface of $TiCl_3$ was covered with thin amorphous layer made by the reaction with moisture or oxygen. Thus, it was expected that the structure and the position of active sites of the Ziegler-Natta catalyst could be observed after protecting the active sites from the damage by the contaminants.

The states of active sites of the $MgCl_2$-supported Ziegler catalyst was investigated with both kinetics and physical analysis. It was suggested by kinetics of propene polymerization with a stopped-flow method that propagation rate constant of isospecific active sites was essentially the same in spite of the co-catalyst used. Thus, it was considered the co-catalyst did not participate directly in the structure of the active sites. Relationship between the oxidative states of the titanium species and the polymerization activity was investigated by XPS analysis and kinetics. The decay of the catalyst during the propene polymerization were found to be related to the variation of oxidative states of the titanium species.

Keywords: Ziegler-Natta catalyst, titanium species, X-ray photoelectron spectroscopy, scanning Auger electron microscopy, transmission electron microscopy, propene polymerization, kinetics