Novel surface alkylated SiO_2-supported Ziegler catalyst for polyethylene with controlled molecular weight distribution

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The industrial polyolefin market is still growing, and new grade polymer has been developed with high performance. For polyethylene, although molecular weight distribution (MWD) was most important factor for determining the mechanical properties, the control of MWD is not achieved sufficiently yet. Free control of MWD is required in order to enhance the application area of polyethylene. Recently, Terano et al. demonstrated that the modified-polyolefin-supported Ziegler catalyst systems had the special characteristic properties. MWD of polyethylene produced with triethylaluminium as cocatalyst was extremely broad ($M_w/M_n > 100$), which is worthy for the industrial aspect because of the significant advantage of broad and/or bimodal MWDs. Furthermore, polyethylene with narrow MWD ($M_w/M_n \approx 2$) could be obtained by combination with diethylaluminumchloride.

The object of this study was the development of novel supported Ziegler catalyst, which can control the MWD and investigate on the origin of catalyst property of MWD control. One of the objectives of this study is to produce polyethylene with controlled MWD through a state-of-the-art manipulation of SiO_2 supported Ziegler catalyst. SiO_2 is known to be one of the ideal supports with good morphology and thermo-stability for preparation of industrial Ziegler catalysts. The functional groups that can be attached to the polymers can similarly be attached to SiO_2 surface. In the catalyst development, so far, the transition metal complexes can also be incorporated directly onto metal-oxide or –halide surfaces without the need for intervening ligands. In the field of polyolefin industries with Ziegler catalyst systems, supported catalysts have been almost entirely developed using plain inorganic support. By constructing the active species similar to modified-polyolefin-supported Ziegler catalyst on the SiO_2 surface, the polymerization catalyst, which could control the MWD of polymer, will be able to be prepared. This concept has possibility of control the MWD with different alkylaluminum cocatalyst. As a result, the novel surface alkylated SiO_2-supported Ziegler catalyst systems could control the molecular weight and MWD of produced polymer by changing solely the kind of cocatalyst.

The industrial aspects of Ziegler catalyst have been developed to high level. However, the academic aspects of Ziegler catalyst were not understood such as propagation mechanism and active site structure. Especially, the model of active site structure has been discussed whether monometallic active site or bimetallic active site. If the active site could be formed monometallic active site without cocatalyst (only alkylation), that structure would be similar to each other with various cocatalyst. Due to dependence of MWD on the kind of alkylaluminum, the active site structure might be different by using different alkylaluminum cocatalyst. To clarify the active site structure, the dependence of MWD on the kind of alkylaluminum was studied in terms of correlation between MWD and the state of Al species by using ^{27}Al MAS NMR. The existence state of aluminum species on the surface alkylated SiO_2-supported Ziegler catalyst activated by halogen including alkylaluminum cocatalyst form dominantly with 4-membered ring structure with titanium species. However, The formation of 4-membered ring was reduced by increasing the size of halogen from chlorine to iodine.

Conclusively, the novel surface alkylated SiO_2-supported Ziegler catalyst systems could control the molecular weight and molecular weight distribution of produced polymer by changing solely the kind of cocatalyst. Furthermore, the changing of molecular weight distribution was depending on difference of interaction between catalyst and cocatalyst.

The findings of this dissertation will have great significance for further development in olefin polymerization using industrial Ziegler catalyst system.