عنوان مقاله:

Insights into the effect of vanadium on chromium-vanadium Phillips catalysts for the ethylene polymerization

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خلاصه مقاله:

The chromium/vanadium bimetallic Phillips catalysts developed by our research group have been proved to be a promising process to produce bimodal polyethylene using a single-reactor process. The vanadium loading of CrV-1/1, CrV-1/2, and CrV-1/3 has a significant effect on the polymerization activity, product molecular weight (MW), as well as the molecular weight distribution (MWD). Due to the unstable and easy deactivation of vanadium active centers at atmospheric or low (0.4 MPa) reaction pressure [Macromol. React. Eng. 2015, 9, 462–472], the reaction is carried out at 1.0 MPa to strength the V active center on the activities of ethylene homopolymerization, ethylene/1-hexene copolymerization, and the H2 responds properties. The reaction carried out at higher pressure promotes the polymerization activities. With the same amount of cocatalyst, the highest activity of the three Cr-V bimetallic catalysts CrV-1/1, CrV-1/2 and CrV-1/3 decreases with the increase of vanadium loading. The Cr-V bimetallic catalysts require more cocatalyst than the single metal Cr cat. It was found two obvious peaks in the GPC curves of homopolyethylen and ethylene/1-hexene copolymer. It means that the higher reaction pressure benefits the promotion of the active center of catalyst for higher MW. By increasing the loading from 0.48 wt.% (CrV-1/1) to 0.96 wt.% (CrV-1/2), the molecular weight increases by nearly 30%. Besides, according to the deconvolutions of the GPC curves of homopolymers, ethylene/1-hexene copolymers, and the homopolymers with H2 modulation, the synergetic effect between Cr and V center is presented. As the vanadium loading increases, the active site accounted for the high molecular weight portion increases, and the Cr-V catalyst presents better hydrogen responds. When the partial pressure of hydrogen is 0.1 MPa, the molecular weight is reduced by nearly half. Specifically, the high molecular weight peak is weakened, while the low molecular weight peak is strengthened. The peak position does not change significantly. The higher vanadium content and the greater sensitivity of hydrogen modulation indicate that the vanadium active center has better hydrogen responds than the chromium active center does. The homopolymerization product of the Cr/V-1/1 catalysts exhibits higher tensile strength and elongation-at-break. The tensile properties of the copolymerized product of CrV-1/1 are further improved.

کلمات کلیدی:
Bimodal polyethylene, Cr-V Phillips catalyst, vanadium loading, GPC, deconvolution analysis