catalysts

MDPI

Supplementary Material for Article

Fragmentation-oriented Design of Olefin Polymerization Catalysts: Support Porosity

Adriano G. Fisch *

Department of Chemical and Materials Engineering. University of Alberta. 9211 – 116 St., Edmonton, Alberta, T6G 1H9, Canada; fisch@ualberta.ca

Abstract: The development of catalysts for the production of polyethylene and polypropylene is ordinarily accomplished on a trial-and-error experimentation program. From the point-of-view of the fragmentation performance, support porosity is the key property affecting the support mechanical resistance and, therefore, it determines the fragmentation process during the early moments of polymerization. The design of the support porosity can be more accurately determined by applying the theoretical knowledge acquired from previous research but which is not consolidated for catalyst design. In this article, it is reported a methodology to optimize the support porosity using a simple fundamental model of the fragmentation process. Using this approach, the design of fragmentation-oriented supports can be achieved for polymerization reactors.

Keywords: Ziegler-Natta; Metallocene; Fragmentation; Polyethylene; Polypropylene

1. Deduction of the Fragmentation Index

The deduction of the fragmentation index is described in Equations S1-S8. The definitions of pore volume (V_{pore}) and skeleton volume (V_{wall}) are given in Equations S1-S2. These equations are redefined in the function of a new variable, particle radius (r) using the definition of the particle volume (V_{part}) in Equation S3 and the chain rule as shown in Equations S4-S5.

$$\frac{\partial V_{pore}}{\partial V_{part}} = \phi(r) \quad \text{(S1)}$$

$$\frac{\partial V_{wall}}{\partial V_{part}} = 1 - \phi(r) \quad \text{(S2)}$$

$$V_{part} = \frac{4}{3}\pi r^3 \quad \text{(S3)}$$

$$\frac{\partial V_{pore}}{\partial r} = \frac{\partial V_{pore}}{\partial V_{part}}\frac{\partial V_{part}}{\partial r} = \phi(r) 4\pi r^2 \quad \text{(S4)}$$

$$\frac{\partial V_{wall}}{\partial r} = \frac{\partial V_{wall}}{\partial V_{part}}\frac{\partial V_{part}}{\partial r} = \left(1 - \phi(r)\right) 4\pi r^2 \quad \text{(S5)}$$

Similarly, the energy accumulated in pores due to the confinement of polymer (E) and the ultimate mechanical strength of the material (λ) are redefined in r, as demonstrated in Equation S6-S7.

$$\frac{\partial E}{\partial V_{pore}} = \frac{\partial E}{\partial r}\frac{\partial r}{\partial V_{pore}} = \frac{1}{\phi(r)4\pi r^2}\frac{\partial E}{\partial r} \tag{S6}$$

$$\frac{\partial R}{\partial V_{wall}} = \frac{\partial R}{\partial r}\frac{\partial r}{\partial V_{wall}} = \frac{1}{\left(1-\phi(r)\right)4\pi r^2}\frac{\partial R}{\partial r} \tag{S7}$$

The definitions in Equations S6-S7 are used in the fragmentation index (Γ_D) along with Equations 5-7 of the manuscript text. The final expression for the Γ_D is presented in Equation S8.

$$\Gamma_D = \frac{\frac{\partial E}{\partial r}}{\frac{\partial R}{\partial r}} = \frac{\phi(r)4\pi r^2 \frac{\partial E}{\partial V_{pore}}}{\left(1-\phi(r)\right)4\pi r^2 \frac{\partial R}{\partial V_{wall}}} = \frac{\phi(r)}{1-\phi(r)}\frac{P}{\lambda(r)} \tag{S8}$$