Counting of Active Centers in Ethylene and Propylene Polymerization with Homogeneous Metallocene Catalysts: Influence of Time in the Initial Stage

10² [C*]/[Zr] (%)

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Introduction

Active centers concentration, [C*], is a key parameter to understand mechanism of olefin polymerization. Various methods for counting C* have been proposed for decades. The method of quenching reactions with acyl chloride compounds, which was first introduced by our group, has been developed a lot. When 2thiophenecarbonyl chloride (TPCC) is applied in quenching ethylene and propylene polymerization, where sulfur tagging carbonyl product can be formed. By measuring the sulfur content of quenched polymer, $[C^*]$ and k_p of the polymerization can be calculated. Using racethylenebis (indenyl)zirconium dichloride (rac-EBIZrCl₂) as catalysts and multiple cocatalysts, here we study the changes of [C*] and $k_{\rm p}$ in the initial stages of ethylene and propylene polymerization.



Scheme 1. Quenching reactions of the active centers by 2-thiophenecarbonyl chloride.

Results and discussion



propylene polymerization research using rac-EBIZrCl₂ at 50 °C , Al/Zr = 1000, TPCC/Al = 2, quenching time = 5 min, 1 atm propylene, cocatalyst: MMAO, n(Zr) $= 1.25 \ \mu mol.$



Fig. 1. Influences of time on activity in ethylene polymerization research using rac-EBIZrCl₂ at 50 °C, Al/Zr = 1000, TPCC/Al = 2, quenching time = $5 \min 1$ atm ethylene and a: cocatalyst: MMAO, n(Zr) = 1.25 µmol; b: cocatalyst: dMAO, $n(Zr) = 1.25 \ \mu mol;$ c: cocatalyst: dMAO,







Fig. 4. Influences of time on C* and observed k_p in propylene polymerization research using rac-EBIZrCl2 at 50 °C, Al/Zr = 1000, TPCC/Al = 2, quenching time = 5 min, 1 atm propylene, cocatalyst: MMAO, $n(Zr) = 1.25 \mu mol.$

t (min)



A diffusion barrier can be used to explain the phenomenon that the observed $k_{\rm p}$ decreased dramatically as the polymerization progressed in Fig. 3 and 4. For the polyethylene or polypropylene layer that rapidly formed in the start-up period covered the catalyst particle, the so-formed diffusion barrier hindered the active center from contacting monomer. C* can rapidly reached to a high level when the cocatalyst contains triisobutyl aluminum. When the system was free of alkyl aluminum, as shown in Fig. 3b and 3c, the increase in C* with time became smoother, and in this system C* kept continuously increasing during the selected polymerization period. For low catalyst concentration in Fig. 3c, C* was easier to approach to a higher value. In the ethylene polymerization system, the number of active centers were higher than that in the propylene system.

Conclusions

Different changes of k_p as well as [C*] with polymerization time were observed in the systems where different cocatalysts were applied. In the MMAO activated system, k_p dropped rapidly while [C*] quickly approached to a platform. Whereas in the dMAO system, [C*] smoothly increased with time. Increasing diffusion barrier can be a reasonable explanation. [C*] was higher in ethylene polymerization than in propylene polymerization.

Acknowledgements

This work was supported by the MOE Key Laboratory of Macromolecular Synthesis and Functionalization.

References

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