Tuning the Cr(III) and Cr(II) Population in Cr/SiO₂ Phillips-type Ethylene Polymerization for Controlling the Catalyst Activity, Induction Period and Polymer Properties

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The Cr/SiO₂ Phillips catalyst has taken a central role in ethylene polymerization ever since its discovery in 1958. This catalyst is unique compared to other ethylene polymerization catalysts since it is active without the addition of a metal-alkyl co-catalyst.[1] Metal-alkyl co-catalysts can, however, be added for the scavenging of poisons, removing the induction period, enhancing the catalyst activity and controlling the polymer products. Despite extensive research into this catalyst working state, still no consensus has been reached. Research has always been hindered by two major reasons: first of all, only a low Cr weight-loading of max. 1% is viable, and second, a proposed maximum of 30% of the Cr-sites is active in ethylene polymerization. Fortunately, with ever advancing spectroscopic and microscopic techniques these two limitations are becoming less of a problem.[2-5] Here we present a study in which the role of metal-alkyl co-catalysts in Phillips-type ethylene polymerization was studied, as schematically illustrated in figure 1A. Industrial batch ethylene polymerization reactions were used for studying the influence of the type, and amount, of metal-alkyl co-catalyst on the catalyst activity and the induction period. More importantly, the findings from these batch polymerization reactions were rationalized by using specially designed in situ UV-Vis-NIR Diffuse Reflectance Spectroscopy experiments for studying of the Cr oxidation state during reduction, in the absence and presence of metal-alkyl co-catalysts, and during subsequent ethylene polymerization. Our results, as schematically illustrated in figure 1B, demonstrate the possibility of controlling Cr(II) and Cr(III) populations by varying the amount, and, type of co-catalyst: ultimately demonstrating the ability to control the catalyst activity, the induction period and also the polymer product properties.

Figure 1. Schematic overview of the research in which we studied A) the influence of the type and amount of metal-alkyl co-catalyst in Phillips-type ethylene polymerization on B) the Cr oxidation state and on catalyst properties such as induction period and catalyst activity. Ultimately demonstrating the possibility rationalizing Catalyst Bulk properties (i.e. catalyst activity and induction period) by carefully controlling the reduction of Cr(VI) surface sites.


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