Surface Science Model Approach to Ziegler-Natta Catalysts

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Introduction

Highly active $MgCl_2$-supported catalysts, containing $MgCl_2$, $TiCl_4$, and an "internal" electron donor, play a significant role in poly(propylene) (PP) production. In combination with a trialkyl aluminum co-catalyst and in most cases an "external" electron donor, they are highly active systems for the production of isotactic poly(propylene). To improve the understanding of state-of-the-art $MgCl_2$-supported catalysts**,** relating to polymerization behaviour and the effect of catalyst type on polymer composition and properties, detailed insight into the nature of the active species is required. The aim is to develop a realistic model for a Ziegler-Natta system that allows a detailed study of surface chemistry and morphology, employing surface science techniques (XPS, SIMS) and microscopy (AFM, SEM). This has been achieved by the spin coating of a $MgCl_2$/donor solution onto a flat Si wafer [1], followed by controlled crystal growth to give well-defined $MgCl_2$ crystallites in which the relative proportions of 120 and 90 degree edge angles indicate the preference for the formation of a particular crystallite face [2, 3].

Materials and Methods

All manipulations of air- or water-sensitive compounds were carried out using standard Schlenk or glove box techniques. The $MgCl_2$·*n*EtOH support and SiO_2/Si(100) wafer used in this work were prepared as described previously [1]. The donors used were 9,9-bis(methoxymethyl)fluorene, diisobutyl phthalate and ethyl benzoate. The donor was added to a solution of $MgCl_2$ in ethanol (42 mmol/L); in the case of the diether donor, the mixture was heated at 60 ˚C until the solution became clear. The donor/$MgCl_2$ molar ratio was 0.1 in the case of the diether donor, 0.1 in the case of bidentate donor DIBP and 0.2 for the monodentate donor EB. The resulting solutions were used to spin-coat a silicon wafer. The spin-coating technique is described elsewhere [1].

Results and Discussion

A fundamental question in Ziegler-Natta catalysis is which crystallite face is most effective for coordination of the active site precursor, $TiCl_4$, and where the active species are located. Treatment of the $MgCl_2$/Donor crystallites with $TiCl_4$, $AlEt_3$ and propylene, followed by the application of Scanning Electron Microscopy and Atomic Force Microscopy, has clearly revealed polymer growth at the edges of the $MgCl_2$ crystallites. In particular, the objective of this work is to investigate to what extent the formation of a particular crystallite face of $MgCl_2$ is dependent on the type of internal donor present during the formation of the support, and ultimately how this affects the location and nature of the active species present in Ziegler-Natta catalysts for poly(propylene). The characteristics of magnesium chloride supports generated in the synthesis of Ziegler–Natta catalysts are strongly dependent on the type of electron donor present in support and catalyst. Comparison of the effects of diether and ester donors in the controlled growth of $MgCl_2$ crystallites, following spin-coating of $MgCl_2$·donor·*n*EtOH from ethanol solution onto a flat silicon wafer, reveals that the presence of a diether leads to the formation of well-defined $MgCl_2$ crystallites in which the presence of only 120◦ (figure 1 left) edge angles indicates a strong preference for the formation of a particular crystallite face. In contrast, the use of a monoester or diester as internal donor generates crystallites with 120◦ and 90◦ edge angles, indicating the presence of both the (110) and the (104) edge surfaces of $MgCl_2$ (figure 1, right). Polymer growth takes place at the edges of the crystallites. The high activity and relatively uniform nature of the active species in catalysts of type $MgCl_2$/$TiCl_4$/diether is likely to be due to preferential formation of the (110) face of $MgCl_2$ when using a diether as internal donor in catalyst preparation.

Significance

Surface science approaches to study Ziegler-Natta catalysts have very successfully been explored by Somorjai and coworkers using UHV methods of preparation [4]. Preparing such model systems by wet chemical impregnation via spin coating has the advantage that the model resembles its industrial counterpart closely. Owing to the planar structure, a range of tools becomes available that cannot be used on industrial catalysts. In this way polymer properties and mechanistic issues can be investigated that were before not accessible.

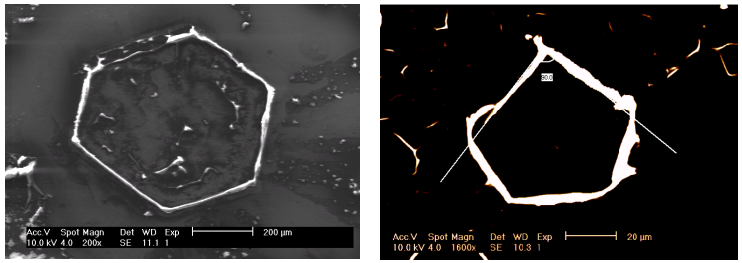

Figure 1. (left) After polymerization (using a diether as internal donor) polypropylene has formed at the edges (120^0 angles) of the $MgCl_2$ crystals. (right) After polymerization (using ethyl benzoate as internal donor) polypropylene has formed at the edges (120^0 and 90^0 angles) of the $MgCl_2$ crystals.

References

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