

Ethylene polymerization over TiSSP composite-supported MAO with bis[*N*-(3-*tert*-butylsalicylidene) cycloheptylamine] titanium dichloride complex

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Received: 21 April 2017 / Accepted: 23 September 2017 / Published online: 30 September 2017
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Abstract The following study focuses on the reduction of the required amounts of MAO after the addition of Ti into the prepared spherical silica particle (SSP) to obtain TiSSP as a support of the bis(phenoxy–imine) Ti-based catalyst used for ethylene polymerization. The ethylene polymerization was carried out via the introduction of SSP and TiSSP-supported MAO with various MAO contents, followed by adding the bis(phenoxy–imine) Ti-based catalyst. The characteristics of SSP and Ti-modified SSP were determined by XRD, BET, FTIR, and NH₃-TPD. There was evidence of the presence of Ti–O–Si bond and the increase of acidity with the introduction of Ti into SSP. Interestingly, the increased acidity on the surface of TiSSP composites was found to be the crucial characteristic, which played an important role on the reduction of the required amounts of MAO. It is suggested that the modification of SSP with Ti is able to decrease (by ca. 22%) the consumption of the required amounts of MAO for polymerization. In other words, the lower ratio of MAO to catalyst for TiSSP was observed for the identical value of activity obtained from SSP. The produced polymers were thoroughly identified by DSC and SEM techniques. All polyethylenes obtained using TiSSP exhibited higher crystallinity than those obtained from SSP support. Finally, employing the TiSSP-supported bis(phenoxy–imine), Ti-based catalyst leads to producing the polymer with lamellar structure that seemed to be

corresponding to the crystalline structure as was confirmed by DSC results.

Keywords Bis(phenoxy–imine) · FI catalyst · Ti–Si composites · Ethylene polymerization

Introduction

In recent years, single-site catalysts have attracted special attention of researchers owing to their structure variation and considerable potential in the polyolefin industry. These catalysts are usually investigated via a simple homogeneous system, which exhibits high activities. Usually, to achieve high activity, the ratios of cocatalyst to catalyst (Al/M) are required to be higher in olefin polymerization for unsupported catalysts. As such, methylaluminoxane (MAO) was reported to be an excellent cocatalyst for single-site catalyst systems [1, 2].

However, one of the most notable drawbacks of the increased use of MAO leads to the considerable increase in cost compared to the use of the conventional aluminum alkyls. Nevertheless, the increased cost may be offset if the amount of MAO employed in the process is reduced and replaced with aluminum alkyls. Despite its high cost, MAO has been remained the most widely used cocatalyst for single-site catalysts. Typically, MAO acts as a spacer group due to its ability to be fixed through the surface hydroxyl groups of the support [3]. Recent studies reported a new immobilization method by introducing spacer groups such as silane [4, 5], Ga and BCl₃ [6], or titania [7–9] between support and catalysts, as shown in Scheme 1.

Today, there is an increased focus on the development of the supported single-site catalyst systems, due to industrial considerations and exploit of their real commercial

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