



# Polymerization of ethylene with $(n\text{BuCp})_2\text{ZrCl}_2$ supported over mesoporous SBA-15 functionalized with sulfonic acid groups

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## ABSTRACT

The polymerization of ethylene in *n*-heptane with  $(n\text{BuCp})_2\text{ZrCl}_2$  supported over mesoporous SBA-15 catalysts functionalized with propyl or aryl sulfonic acid groups and impregnated with either MAO or TMA was investigated and compared with reference samples. All the supports showed mesoscopic ordering with pore sizes of 7.8–6.6 nm, BET surface areas around  $700\text{ m}^2\text{ g}^{-1}$ , sulfonic acid loadings between 10 and 20 wt% and an acidity of roughly  $1\text{--}1.7\text{ mmol H}^+\text{ g}^{-1}$ . None of the catalysts were capable of polymerizing ethylene in the absence of MAO in spite of using TMA or TIBA as scavengers. The addition of MAO (Al/Zr = 800 or 5000) led towards ethylene polymerization, being the activity dependent on Al/Zr molar ratio (higher for Al/Zr = 5000). The catalysts treated with TMA during the impregnation exhibited considerable leaching, unlike those treated with MAO wherein the leaching was low (<9 wt%). The presence of the sulfonic acid moiety enhanced the activity of the catalysts. In addition, the activity was also augmented with the increase of the sulfonic acid content from 10 to 20 wt%. Interestingly, the molecular weight of the polyethylene synthesized with the SBA-15 functionalized with sulfonic acid groups were 1.5–2.5 times higher, especially with the propyl moiety which leads towards  $M_w \sim 350,000\text{ g mol}^{-1}$  at 1.2 barg. The results were explained through an interaction between the sulfonic acid moiety and the chlorinated MAO species, which activates the metallocene.

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## 1. Introduction

Metallocene compounds comprise a versatile group of organometallic catalysts for olefins polymerization [1]. In fact, their discovery represented a major breakthrough compared with conventional Ziegler–Natta [2] and Philips catalysts due to the remarkable properties showed by the products obtained [3,4]. These differences have been related to the presence of uniform catalytic sites which lead towards narrow molecular weight distributions, with polydispersity indexes close to 2 [5–7]. In addition, when dealing with the copolymerization of ethylene with  $\alpha$ -olefins, the metallocene catalysts allows a uniform distribution of the branches independently of the molecular weight [8,9]. Another advantage of metallocene catalysts over Ziegler–Natta ones is the possibility to incorporate long chain  $\alpha$ -olefins, whose presence in low loadings (around 1 wt%) provides the polyethylene with interesting properties for industrial processing (e.g. better tearing toughness) [10]. Finally, since the molecular weight of the polymer depends mostly on the molecular structure of the

metallocene, even ultra high molecular weight polyethylene (UHMWPE,  $10^6\text{--}10^7\text{ g mol}^{-1}$ ) may be prepared by a suitable design of the metallocene molecule [11].

Homogeneous polymerization with metallocene catalysts originates ill defined morphologies of the product particles and usually, reactor fouling. The industrial application of the metallocene catalysts typically requires their immobilization over different supports in order to use them in the conventional slurry and gas phase industrial processes [12]. In literature can be found many examples of application of different carriers for supporting metallocenes: zeolites [13,14], silica [15–18], alumina [19,20], clay [21], cyclodextrin [22], synthetic polymers [23,24] and mesoporous materials (SBA-15, MCM-41) [25,26]. The latter show the advantage of a better dispersion of the active phase (metallocene) over the support due to their uniform mesopore size and high surface area ( $600\text{--}1200\text{ m}^2\text{ g}^{-1}$ ), reducing the formation of polynuclear species by metallocene condensation reactions. Both the nature of the support and the procedure of supporting the metallocene affects to the catalytic activity and the properties of the polymer. In general, the activity of supported heterogeneous systems is lower than the homogeneous ones due to the occurrence of diffusion constraints as well as to the deactivation of numerous active sites on supporting. However, the latter pitfall can be overcome by means of special procedures such as the patterning methodology which enable to

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