



2D-aluminum-modified solids as simultaneous support and cocatalyst for *in situ* polymerizations of olefins

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ABSTRACT

The reaction of methylaluminoxane (MAO) with 2D and 3D inorganic supports such as magadiite, [Al]-magadiite, *n*-alkyl-AlPO-kanemite, MCM-41 and MCM-48 was investigated by solid state NMR spectroscopy. The products obtained from the reaction of aluminum-modified magadiite and MAO were dominated by surface species of the type Si—OCH₃/Al—OCH₃. A mechanism for the surface reactions of MAO is proposed. The MAO-modified solids were employed for the polymerization of ethylene with constrained geometry catalyst (CH₃)₂Si(C₂₉H₃₆)(N¹-Bu)ZrCl₂ (1). This constrained geometry catalyst produced remarkably high activity comparable to the homogeneous system. MAO-modified [Al]-magadiite seems to have an increased acidity. [Al]-magadiite as well as *n*-alkyl-AlPO-kan, when employed as supports for Ph₂C(C₅H₄)(C₂₉H₃₆)ZrCl₂ (2), kept a constant activity at low cocatalyst/Zr ratios whereas pure-silica supports led to a rapid decay in activity. Transmission electron microscopy (TEM) confirmed the formation of PE nanocomposites on magadiite-supported catalyst 2.

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1. Introduction

Since the discovery and initial use of methylaluminoxane (MAO) by Kaminsky [1], which caused olefin polymerization activities to reach values of 10,000 times higher than using trimethylaluminum (TMA), MAO has played an essential role in polyolefin research. In 2015, 184 million metric tons (Mt) of polypropylene (PP) and polyethylene (PE) have been synthesized by old and new polymerization systems; this corresponds to about 48% of the global plastic production (381 Mt) [2].

Although there are advantages of homogeneous metallocene catalysts, such as high activity and stereoregularity, there are also some critical problems that hamper the commercial applications such as the instabilities of slurry or gas phase processes and the large quantities of methylaluminoxane that are required [3]. To overcome these problems, silica, alumina, MgCl₂ or clays are usually employed to heterogenize the homogeneous catalyst and allow them to be employed at a large-scale facility. Supported metallocene catalysts can be prepared by several methodologies [4–7]. One of the employed methods are based on the direct

immobilization of metallocene onto the inorganic oxides [8–11]. Detrimental interactions of the catalysts with the surface of the support can be avoided by pretreating the support with the cocatalyst prior to metallocene anchoring [12]. Some suggestions have been reported in the literature for the preparation of MAO-modified silica using chemisorption of MAO or *in situ* preparation by reacting trimethylaluminum (TMA) with silica, for example [13]. Other approaches involve reactions of silica modified with organosilanes [14], the use of polymers [15], as well as inorganic-organic hybrid xerogels [12,16,17]. Each of these strategies affords different catalyst performances and produces polyolefins with different properties and particle morphology.

Moreover, the presence of a very small amount of nanofiller adds to the polymer matrix a substantial change in physical and mechanical properties. Since Toyota's pioneering work on polymer layered silicate nanocomposites [18], layered materials have shown to be interesting supports. They can impart to the polymer a substantial increase in mechanical properties, thermal stability, fire resistance, and gas diffusion barrier for example. Previous works have shown that the polymerization of olefins using *n*-alkyl-AlPO-kanemite, a layered aluminumphosphate with kanemite structure, as a support for *rac*-Et[Ind]₂ZrCl₂ in the *in situ* polymerization of propylene resulted in polypropylene nanocomposites with a superior degree of exfoliation of the filler [19]. At the same time, reaction of an organomodified

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aluminophosphate with MAO caused extensive changes in the solid including the reaction with the interlayer organic moieties, elimination of part of it, and material delamination.

The nature of the active site for polymerization on metallocene/MAO and the role of MAO are not fully understood especially when it is supported on a silica surface [20]. Even today, the exact structure of MAO during polymerization is not fully known because there are equilibria among the oligomers $[-Al(CH_3)O-]_n$, as well as complexation with each other and with unreacted TMA [21]. MAO is a compound in which aluminum and oxygen atoms are interpolated and free valences on Al are saturated by methyl substituents [22]. As the aluminum atoms in the unit structures of MAO are coordinatively unsaturated, the units join together forming clusters and cages. One of its functions is the alkylation of the metallocene complex when a dichloride is used. Recently, some groups [23–27] have been dedicating efforts to understand the composition and role of methylaluminumoxane on the presence of silica. Using spectroscopy and computational approaches they found that one of the role of MAO in the supported metallocene-based olefin polymerization catalyst is to provide $AlMe_2^+$ species, originating from weak Lewis acid sites which are the main species for metallocene activation. The other role is to scavenge all surface hydroxyl groups as the main cause for deactivation.

Having this context in mind, the present work proposes to shed some light on the effects that MAO can have on supports like magadiite, AIPO-kanemite and mesoporous solids (MCM-41 and MCM-48) when heterogeneous sterically expanded cyclopentadienyl metallocenes are employed for polyolefin synthesis. Also, reported and discussed is the effect that the framework aluminum/layered carriers have on the

catalytic behavior of the system using moderate MAO:Zr ratios.

2. Experimental

2.1. Synthesis of the inorganic supports

The syntheses of MCM-41 [28], Na-magadiite [29], [Al]-magadiite (Si/Al molar ratio = 16.4) [30] and n-alkyl-AIPO-kanemite $(AlPO_3(OH)_2[CH_3(CH_2)_{11}NH_2]_{0.43}[CH_3(CH_2)_3NH_2]_{0.57} = 43 \text{ dod}, 57 \text{ but-AIPO-kan})$ [31] followed procedures developed previously from our group. For MCM-48 synthesis, the procedure reported by Castruita et al. [32] was followed. All the solids were pre-treated for 12 h at 100–200 °C under vacuum ($\sim 10^{-5}$ mbar) prior to the organic modifications. The support's structures are represented in Fig. 1.

2.2. Supported MAO

Initially, ~ 50 mg of support, previously dried under vacuum at 150 °C for 12 h, was dispersed in 25.0 mL of anhydrous toluene and ~ 0.2 g of solid MAO was added to the suspension. This load was calculated to afford a Al/Zr molar ratio in the reactor equal to 1000. In order to investigate the role of MAO on the support under the conditions employed in this work, the following math was considered:

For example, 40.6 mg of 2@MCM-48 gives $[Zr] = 3.37 \mu\text{mol}$ (see Table SI_02 in ESI). For MAO/Zr = 1.000, 3.37 mmol of MAO were necessary. The MW of MAO used in this work was 57.958 g/mol, so the amount of solid MAO necessary for the reaction was 0.195 g.

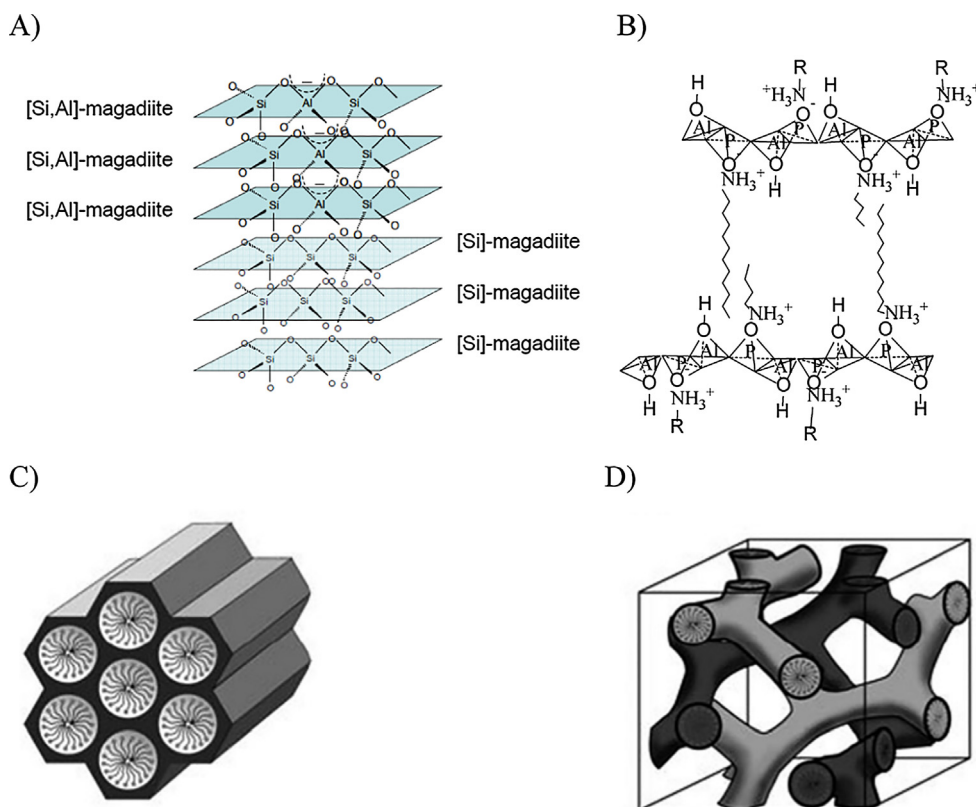


Fig. 1. Representation of supports' structures. (A) Magadiite and [Al]-Magadiite lamella. (B) n-alkyl-AIPO-kanemite. (C) MCM-41 and (D) MCM-48. Reproduced with permission of [30,33]. The structure of magadiite was simplified because its structure remains unknown.

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