



The role of electron donors on lateral surfaces of MgCl₂-supported Ziegler–Natta catalysts: Observation by AFM and SEM

Adelaida Andoni^{a,b}, John C. Chadwick^{b,c}, Hans J.W. Niemantsverdriet^{a,b}, Peter C. Thüne^{a,b,*}

^a Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

^c Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 14 February 2008

Revised 11 April 2008

Accepted 11 April 2008

Available online 22 May 2008

Keywords:

Model catalyst

Ziegler–Natta catalysis

Electron donors

Morphology

Atomic force microscopy

Scanning electron microscopy

ABSTRACT

An active model for a Ziegler–Natta propylene polymerization catalyst has been prepared by spin-coating of a MgCl₂/diether donor solution in ethanol on a flat silicon wafer, followed by crystal growth by Ostwald ripening to give well-defined MgCl₂·donor·*n*EtOH crystallites. The growth of the crystallites on the flat wafer indicates the formation of only 120° edge angles in the presence of the diether donor, suggesting the preference for the formation of one particular crystallite face for the MgCl₂. In contrast, the presence of diisobutyl phthalate or ethyl benzoate leads to the formation of both 120° and 90° edge angles, indicating the formation of more than one face for the MgCl₂. Subsequent treatment with TiCl₄ generates the catalyst and in propylene polymerization polymer forms on the lateral face of each crystallite. This work represents the first visualization of the effect of an internal donor in controlling the crystallite faces of magnesium chloride formed during a Ziegler–Natta catalyst preparation.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Highly active MgCl₂-supported catalysts, containing MgCl₂, TiCl₄, 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). Successive “generations” of highly active MgCl₂-supported catalyst systems for PP are listed below Table 1 [1].

The internal donor plays an important role in controlling the amount and the distribution of TiCl₄ in the catalyst. Giannini [2] indicated that on the lateral cleavage surfaces of MgCl₂, the magnesium atoms are coordinated with 4 or 5 chlorine atoms, as opposed to 6 chlorine atoms in the bulk of the crystal. These cleavage

surfaces were assigned to the (110) and (100) faces of MgCl₂. It has been proposed that bridged Ti₂Cl₈ species can coordinate to the (100) face of the MgCl₂ and could lead to the formation of the chiral, isospecific active species [3,4]. Preferential coordination of a donor on the more acidic (110) face of MgCl₂ would therefore lead to the (100) face being prevalently occupied by Ti₂Cl₈ dimers. However, recent mechanistic and modeling studies, in particular spectroscopic studies using FT-Raman [5,6], have provided evidence for strong adsorption of TiCl₄ on the (110) lateral cut of MgCl₂, giving a monomeric species with octahedrally coordinated titanium which can be the precursor for active and stereospecific sites. Good performance in terms of stereospecificity can be reached only by preventing the displacement of the internal donor coordinated to MgCl₂. Internal donors such as ethyl benzoate and diisobutyl phthalate are, to a large extent, removed from the support by alkylation and complexation reactions with the AlR₃ co-catalyst, necessitating the use of an external donor in the polymerization [7]. In contrast, diethers such as 2,2-disubstituted-1,3-dimethoxypropanes remain strongly coordinated to the support when the catalyst is brought into contact with the co-catalyst, so that high stereospecificity can be obtained even in the absence of an external donor [8]. Modeling studies carried out by Barino and Scordamaglia [9] have indicated that the 1,3-diethers giving the greatest stereoregulating effect are those which have the greatest preference for coordination on the (110) rather than the (100) face of MgCl₂.

Table 1

Evolution of Ziegler–Natta catalysts with internal/external donors

Catalyst	Co-catalyst	External donor
MgCl ₂ /TiCl ₄ /ethyl benzoate	AlR ₃	Aromatic ester
MgCl ₂ /TiCl ₄ /dialkyl phthalate	AlR ₃	Alkoxy silane
MgCl ₂ /TiCl ₄ /diether	AlR ₃	

* Corresponding author at: Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. Fax: +31 40 247 3481.

E-mail address: p.c.thuene@tue.nl (P.C. Thüne).

Very recently, the crystal structure of MgCl_2 supports has been re-evaluated by Busico et al., who concluded that the surface with five-coordinate Mg cations should be indexed as (104) rather than (100) [10]. Periodic DFT calculations indicated that the (104) surface has relatively low energy and is the dominant lateral surface in well-formed large crystals, as well as in activated supports prepared by ball milling. It was also shown that a monodentate alkoxy silane donor $\text{RMe}_2\text{Si}(\text{OMe})$ was able to bind to both the (104) and the (110) edge surfaces, whereas a bidentate alkoxy silane, $\text{RMeSi}(\text{OMe})_2$, was able to bind only on coordinatively unsaturated sites such as those on the (110) surface. In the present work we will adopt the indices (110) and (104), as advised by Busico and co-workers, for the four- and five-coordinate surfaces, respectively [10].

Our own research concerning fundamental aspects of olefin polymerization catalysis has been based on the synthesis and characterization of catalysts on flat silicon wafers. Studies of Phillips catalysts for polyethylene involved atomic force microscopy (AFM) investigation of ethylene polymerization catalyzed by chromium species anchored on a silicon wafer, identifying polymer growth at a nm scale during the early stages of polymerization [11,12]. Recently, we introduced the preparation and characterization of a model Ziegler–Natta catalyst, starting from the spin-coating of a MgCl_2 solution in ethanol on a flat silicon wafer [13]. Subsequent contacts with TiCl_4 and AlEt_3 resulted in an active catalyst for ethylene polymerization, enabling a study of the surface chemistry and morphology of the catalyst and polymer. This first study established the viability of the model Ziegler–Natta catalyst preparation, but did not result in well-defined crystallites of magnesium chloride. Next, we developed a preparation method by which the spin-coated support precursor, $\text{MgCl}_2 \cdot n\text{EtOH}$, could be converted by controlled crystal growth to well-defined MgCl_2 crystallites large enough to facilitate their morphological characterization by AFM and scanning electron microscopy (SEM), and to identify polymer formation on the lateral faces of the crystallite [14].

We utilized the same model for propylene polymerization by firstly incorporating a diether donor in the spin-coating of MgCl_2 from ethanol solution onto a silicon wafer [15]. Crystal growth by Ostwald ripening was applied to generate large crystallites, allowing the effect of the diether to be investigated by morphological characterization of the crystallites by SEM and, after polymerization, by the identification of polymer growth on the lateral faces of the crystallites. Well-defined crystal faces and angles were apparent in SEM images and hexagonal structures and 120° edge angles were evident, irrespective of the amount of diether incorporated into the system. Polymerization experiments clearly revealed polymer growth at the edges of the crystallites.

We have now discovered that the type of internal donor present in the support and catalyst preparation has a profound effect on the formation of different crystallite faces of magnesium chloride. In the present work, we describe the different effects obtained with 9,9-bis(methoxymethyl)fluorene, diisobutyl phthalate and ethyl benzoate, and the implications of these results with respect to the location and nature of the active species present in Ziegler–Natta catalysts for poly(propylene).

2. Experimental

2.1. Materials

Anhydrous magnesium chloride (beads, 99.9%), absolute ethanol (99.9%), titanium tetrachloride (99.9%) and triethylaluminum (25 wt% in toluene) were purchased from Aldrich Chemicals and used as received. HPLC-grade toluene was taken from an argon-flushed column packed with alumina and stored over 4 Å molecu-

lar sieves. The diether donor used was 9,9-bis(methoxymethyl)fluorene [16]. Diisobutyl phthalate ($\geq 98\%$) and ethyl benzoate ($\geq 99\%$) were provided by Aldrich and used as received. Propylene was supplied by Linden (3.5).

2.2. Catalyst preparation and propylene polymerization

All manipulations of air- or water-sensitive compounds were carried out using standard Schlenk or glove box techniques. The $\text{MgCl}_2 \cdot n\text{EtOH}$ support and $\text{SiO}_2/\text{Si}(100)$ wafer used in this work were prepared as described previously [13]. 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 [13].

The spin-coated $\text{MgCl}_2/\text{donor} \cdot n\text{EtOH}$ layer was contacted with ethanol vapor in a closed system for 30 min at 60°C and subsequently at 50°C for 100 min, aiming to convert a large number of small $\text{MgCl}_2/\text{diether} \cdot n\text{EtOH}$ crystallites to a smaller number of larger crystallites via a process of Ostwald ripening. Details of this procedure have already been reported [14]. The $\text{MgCl}_2/\text{donor} \cdot n\text{EtOH}$ crystals were treated with a 10% (v/v) TiCl_4 solution in toluene at room temperature for 30 min. After washing with toluene to remove the physisorbed TiCl_4 , the model catalyst was dried under nitrogen.

Propylene polymerization was carried out at room temperature in a glass reactor equipped with a magnetic stirrer. The silicon wafer, with the model catalyst prepared as above, was dipped into about 20 mL of a 1 mg/mL solution of the co-catalyst, AlEt_3 , in toluene, inside the glass reactor. The reactor was pressurized with 3 bar of propylene and polymerization was allowed to run for the desired time, after which the wafer was washed with toluene.

2.3. Analytical techniques

AFM measurements were performed inside a glove box with a Solver P47 base with SMENA head. The cantilever of choice was a non-contact gold-coated NSG11 (long end), manufactured by MicroMasch. A typical force of the tip was 5.5 N/m and a typical resonance frequency was 164 kHz. The measurements were performed in non-contact mode. The thickness of the catalyst support was determined using the height difference between the Si-substrate and the MgCl_2 surface. SEM was performed using a Philips environmental scanning electron microscope XL-30 ESEM FEG (Philips, The Netherlands, now Fei Co.) in high-vacuum mode using a low voltage (low-voltage SEM, LVSEM) and a secondary (SE) detector. High accelerating voltage and a secondary (SE) detector was used for energy dispersive X-ray (high-voltage SEM-EDX, HVSEM-EDX) analyses.

3. Results

As previously reported [13], spin-coating of a solution of magnesium chloride in ethanol onto a flat silicon wafer results in a solid layer consisting of small grains of $\text{MgCl}_2 \cdot n\text{EtOH}$. AFM images indicated a surface roughness of 1–3 nm with a grain size ranging from 10–40 nm [13]. Spin-coating was carried out under similar conditions in the present work, with the exception that a diether donor, 9,9-bis(methoxymethyl)fluorene, was incorporated into the magnesium chloride solution. A 0.1 molar ratio diether/ MgCl_2 was applied, comparable to that present in a typical

Download English Version:

<https://daneshyari.com/en/article/62423>

Download Persian Version:

<https://daneshyari.com/article/62423>

[Daneshyari.com](https://daneshyari.com)