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A Flat Model Approach to Ziegler-Natta Catalysts for Propylene Polymerization and a Preparation Method of Well-defined Crystallites of $MgCl_2$-supported Catalysts

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Summary: An active model for a Ziegler-Natta propylene polymerization catalyst has been prepared by spin-coating of a $MgCl_2$/diether donor solution in ethanol on a flat silica wafer, followed by crystal growth by Ostwald ripening to give well-defined $MgCl_2 \cdot$ diether $\cdot n$EtOH crystallites. The flat model approach facilitates detailed characterization of the catalyst and polymer using surface spectroscopy and microscopy techniques. The growth of the crystallites on the flat silica indicates formation of only 120° edge angles, suggesting the preference for the formation of one particular crystallite face for the $MgCl_2$. Subsequent treatment with $TiCl_4$ generates the catalyst and in propylene polymerization polymer forms on the lateral face of each crystallite.

Keywords: flat model; poly(propylene) (PP); scanning electron microscopy; spin coating; Ziegler-Natta polymerization

Introduction

Since the discovery of Ziegler-Natta catalysts for ethylene and propylene polymerization, questions regarding which crystallite face of $MgCl_2$ is most effective for coordination of the active site precursor, $TiCl_4$, and where the active species are located, have remained largely unresolved. It has been proposed that dimeric species (Ti_2Cl_8) epitactically coordinated to the (100) lateral cut could lead to the formation of stereospecific active sites.[1,2] However, recent spectroscopic studies using FT-Raman have provided evidence for strong adsorption of $TiCl_4$ on the (110) lateral cut of $MgCl_2$, giving a monomeric species with octahedrally coordinated titanium which can be the precursor for active and stereospecific sites.[3,4] For propylene polymerization, the incorporation of an internal donor (monoester, diester or diether) is required in the catalyst preparation to control the amount and distribution of $TiCl_4$ on the support surface. External electron donors (Lewis bases) are included in the polymerization to produce highly isotactic polypropylene. These donors are also presumed to be coordinated on the lateral cleavages of $MgCl_2$. Good performance in terms of stereospecificity can be reached only by preventing the displacment of the internal donor coordinated to $MgCl_2$ by the co-catalyst AlR_3, a strong Lewis acid present in the polymerization reaction. Diether donors satisfiy this requirement and 1,3-diether donors with general formula **1** can give stereospecific catalysts even

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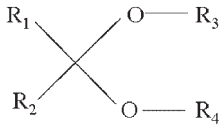
in the absence of an external donor.[5] In other words they remain coordinated to $MgCl_2$ in the presence of $TiCl_4$ and AlR_3.



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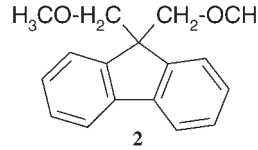
In a previous communication, we introduced the preparation and characterization of a model Ziegler-Natta catalyst, starting from the spin-coating of a $MgCl_2$ solution in ethanol on a flat silicon wafer.[6] Subsequent contacts with $TiCl_4$ and $AlEt_3$ resulted in an active catalyst for ethylene polymerization, allowing a study of the surface chemistry and morphology of the catalyst and polymer. This initial study established the feasibility of the model Ziegler-Natta catalyst preparation, but did not result in well-defined crystallites of magnesium chloride. Subsequently, we identified a method by which the spin-coated support precursor, $MgCl_2 \cdot n$EtOH, could be converted by controlled crystal growth to well-defined $MgCl_2$ crystallites large enough to facilitate their morphological characterization by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), and to identify polymer formation on the lateral faces of the crystallite.[7]

We have now 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 silica wafer. Crystal growth by Ostwald ripening is then 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.

Experimental Part

The $MgCl_2 \cdot n$EtOH support and SiO_2/Si(100) wafer used in this work were prepared as described previously.[6] The diether donor used was 9,9–bis(methoxymethyl)fluorene[8] (**2**). The desired quantities of the diether were added to a solution of $MgCl_2$ in ethanol (42 mmol/L) and heated up to 60 °C until the solution became clear.



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The resulting solution was used to spin-coat a silica wafer. The spin-coating technique is described elsewhere.[6] In the experiments in which Ostwald ripening of the spin-coated support was not applied, the wafer was then dried under nitrogen and used as such for XPS analysis. Grafting of $TiCl_4$ onto the $MgCl_2$/diether $\cdot n$EtOH was carried out by treatment with a 10% v/v $TiCl_4$ solution in toluene at room temperature. After washing with toluene to remove the physisorbed $TiCl_4$, the model catalyst was dried under nitrogen. The flat silica wafer containing the catalytic components can be used for either propylene polymerization or XPS analysis. Both the $TiCl_4$ treatment and the washing step took 30 min.

In the experiments involving Ostwald ripening of the support, the spin-coated $MgCl_2$/diether $\cdot n$EtOH layer was contacted with ethanol vapour 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 $MgCl_2$/diether $\cdot n$EtOH crystallites to a smaller number of larger crystallites. Details of this procedure have been reported elsewhere.[7] Ostwald ripening involves the separation of a second phase from a supersaturated solution. In other words, crystal growth by ''Oswald ripening'' occurs when smaller crystals, which have a larger total area than bigger crystals, dissolve in the liquid phase, after which the material is transported through the continuous phase to nucleation sites on the bigger crystals.[9,10] After this step, the

wafer was left overnight to dry under nitrogen, then treated with $TiCl_4$ as described above.

Propylene polymerization was carried out at room temperature in a glass reactor equipped with a magnetic stirrer. The silica wafer, after deposition of $MgCl_2$/diether · *n*EtOH and treatment with $TiCl_4$, 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 the polymerization was allowed to run for the desired time. After the polymerization, the wafer was washed with toluene and used such as for SEM analysis. Details of materials and analytical techniques used in this work have been published elsewhere.[6]

XPS Analysis of Spin-Coated Supports and Catalysts

A flat model support, prepared by spin-coating of $MgCl_2$/diether · *n*EtOH from ethanol solution onto a flat silicon wafer and subsequent treatment with $TiCl_4$ without first subjecting the spin-coated film to Ostwald ripening, was studied using X-ray photoelectron spectroscopy (XPS).

Figure 1 shows overview XPS spectra of spin-coated $MgCl_2 \cdot n$EtOH films prepared with and without the diether donor and after treatment with $TiCl_4$ of diether-containing film.

In this experiment the diether/Mg molar ratio was 0.1, similar to that in typical Ziegler-Natta catalysts containing this donor.[11] It is apparent on comparing

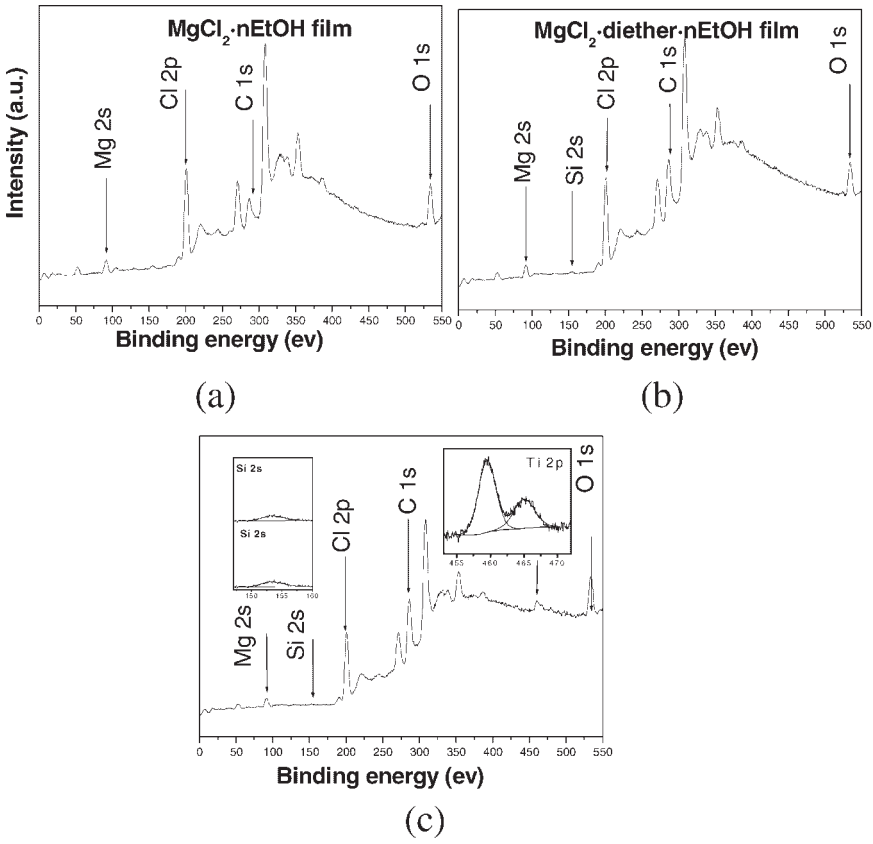

Figure 1.
Wide-scan XPS spectra: (a) and (b) $MgCl_2 \cdot n$EtOH and $MgCl_2 \cdot$ diether · *n*EtOH films respectively (c) after treatment of the diether-containing film with $TiCl_4$. The inserted spectra show the Ti 2p peak and the Si 2s peaks before and after treatment with $TiCl_4$.

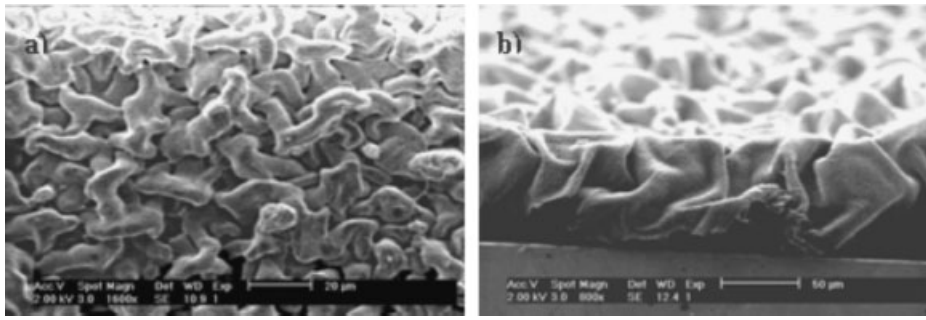

Figure 2.
SEM images of polypropylene obtained after 24 hours polymerization; a) top view; b) side view on silica wafer. polymerization had an M_w of 404,300 g · mol^{-1} and a molecular weight distribution (M_w/M_n) of 8.8. The polymer melting point, determined by DSC, was 153 °C.

Figure 1a and b that, upon addition of the diether donor, the C 1s signal in the XPS spectrum increases. The Mg/Cl ratio in the spin-coated $MgCl_2 \cdot n$EtOH film prepared in the absence of donor was 1.00:1.96, indicating that the magnesium chloride had deposited without any significant hydrolysis.[6] This ratio remained unchanged upon incorporation of the diether donor. The O 1s peak remains significant in the spectra, before and after addition of the donor. Figure 1c shows the XPS spectrum after contacting the $MgCl_2 \cdot$ diether $\cdot n$EtOH support with $TiCl_4$. The inserted spectra show the Ti 2p peak after the contact with $TiCl_4$ and the Si 2s peaks before and after the treatment with $TiCl_4$. The Si/Mg ratio (0.10)[12] does not change upon treating with $TiCl_4$ indicating that the film stays intact. The Mg 2s and Mg 2p emissions showed maxima at binding energy 90.8 eV and 52.0 eV, whereas Cl $2p_{3/2}$ appeared at 199.5 eV. The maximum of the Ti $2p_{3/2}$ emission was at 459.5 eV, typical for Ti (+4). The Ti2p/Mg2s ratio corresponds to a Ti/Mg atomic ratio of 0.2.[12] This ratio remained constant when changing the take-off angle for the photoelectrons from 0^0 to 60^0 relative to the surface, indicating a homogeneous distribution of the Ti in the spin-coated film.

The model catalyst prepared as described above proved to be active for propylene polymerization at 3 bar propylene pressure and room temperature. Polypropylene (PP) is formed, in milligram quantities, as a thin film on the silica surface (3×3 cm^2). No polymer formation was observed in the solution. The thickness of diether-containing film was 25 ± 5 nm. SEM indicated a thickness of the polymer film of $\sim$1 μm after 24 hours polymerization when no donor was incorporated. The film thickness reached up to 50 μm after 24 hours polymerization when diether donor was incorporated into the system. This corresponds to a polymer yield of 1 kg PP/g $MgCl_2$ after 24 hours. Magni and Somorjai[13] reported a turnover frequency of 0.2 molecules/(site.s) for propylene polymerization with a model Ziegler-Natta catalyst, prepared by gas phase deposition of an ultra-thin $TiCl_4/MgCl_2$ film in UHV conditions, at 760 torr and 300 K. Our system has a nominal insertion rate of 0.14 C_3H_6/(Ti atom.s) at 3 bar pressure and room temperature. In the SEM images (Figure 2) the polymer films appear to consist of a mass of elongated particles when viewed from the top. A lateral view, however, clearly reveals that the polymer films consist of a folded layer which is aligned perpendicular to the surface of the support, indicating a vertical growth of the polypropylene film. The polymer obtained after 24 h

Preparation and Characterization of Well-defined Crystallites

Spin-coating of a solution of magnesium chloride and diether in ethanol onto a flat silicon wafer results in a solid layer, which is likely to be comprised of small particles of $MgCl_2$.diether · nEtOH. Aiming to convert this material to well-defined crystallites large enough to be characterized by SEM, the spin-coated layer was subjected to a process of Ostwald ripening as described in the experimental section. Figure 3 represents SEM images taken after propylene polymerizations with model catalysts prepared by subjecting the spin-coated support to Ostwald ripening prior to treatment with $TiCl_4$.

The SEM images of the crystallites after polymerization reveal the presence of relatively large, micron-sized crystallites. Well-defined crystal faces and angles are apparent in these images and hexagonal structures and 120^0 edge angles are evident, irrespective of the amount of diether incorporated into the system. The formation of crystallites with only 120^0 edge angles indicates the exclusive formation of only one crystallite face, i.e. (110) or (100). It may be speculated that the formation of hexagonal crystallites with 120^0 angles indicates the preferential formation of the (110) cut in the presence of the diether, taking into account the strong evidence from modelling studies that the dominant coordination mode of diethers to $MgCl_2$ is via bidentate coordination on the (110) cut.[14,15] In addition to the hexagonal structure, it is noticeable that the crystallites shown in Figure 3b have grown in a particular stacking fashion. The indications from the SEM images of polymer formation on the edges of the hexagonal crystallites are supported by energy dispersive X-ray (EDX) mapping of the C-K_α and Al-K_α distribution after 16 hours polymerization, as shown in Figure 4. Carbon is located predominantly on the corners and edges of the crystallites, although a small amount of polymer appears to be also present on the

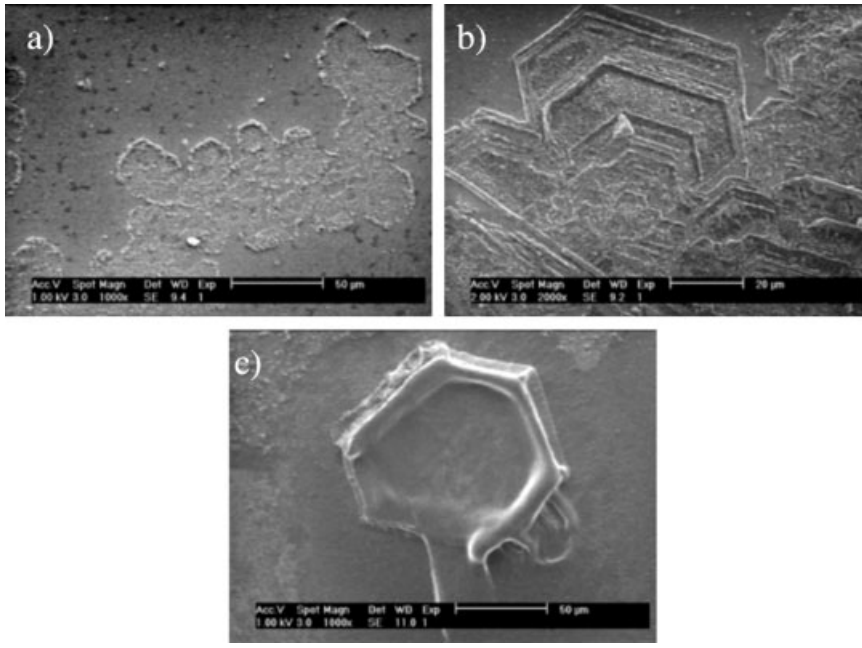

Figure 3.
SEM images of polypropylene obtained after 16 hours polymerization; mol ratio diether/$MgCl_2$: (a) 2; (b) 0.4; (c) 0.1.

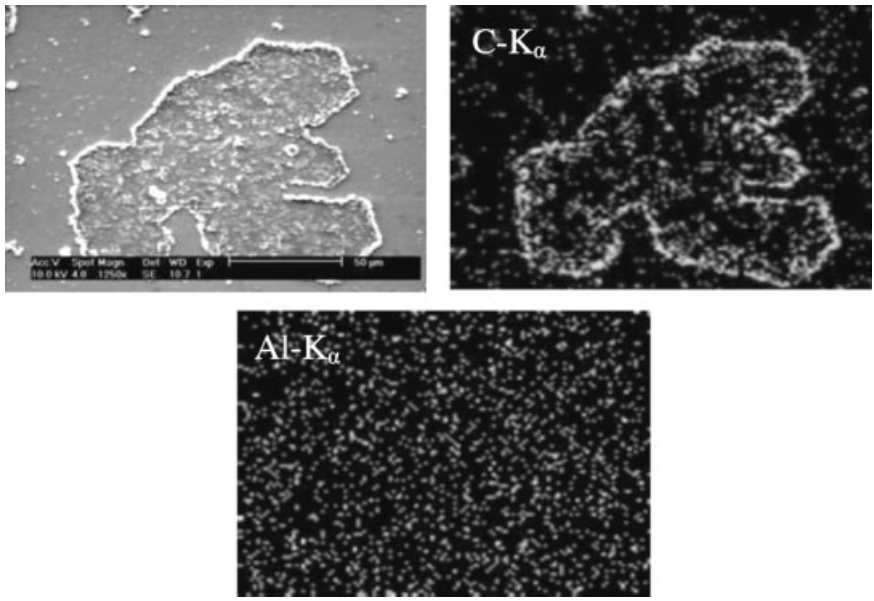

Figure 4.
SEM image and SEM-EDX mapping of C-K_α and Al-K_α of polypropylene obtained after 16 hours polymerization on silica wafer. Diether/$MgCl_2$ molar ratio 0.4.

basal planes of the crystallites. The polymer growth at the edges of the crystallites clearly indicates the presence of the active site precursor, $TiCl_4$ or $TiCl_n(OEt)_{4-n}$. In contrast, Al-K_α mapping indicates that aluminium originating from the co-catalyst is located all over the Si wafer.

In addition, propylene polymerization was carried out without the incorporation of the donor. The spin-coating of a solution of magnesium chloride was subjected to the Ostwald ripening process, followed by treatment with $TiCl_4$ and polymerization for 16 hours under propylene at 3 bar pressure. SEM images (not shown) indicated the formation of both 120^0 and 90^0 edge angles. This suggests that the incorporation of a diether donor ''generates'' exclusively only 120^0 edge angles.

Conclusions

Model Ziegler-Natta catalysts, active in propylene polymerization, can be prepared from supports obtained by the spin-coating of $MgCl_2$/diether $\cdot$ *n*EtOH from ethanol solution onto a flat silica wafer. The flat model is valuable as it allows a surface chemistry and morphological study of the catalyst and nascent polymer, employing microscopy techniques (SEM) as well as surface science techniques such as XPS.

A method for the preparation of well-defined crystallites of $MgCl_2$-supported Ziegler-Natta catalysts has been established. Treatment of the crystallites with $TiCl_4$, $AlEt_3$ and propylene resulted in a system active in propylene polymerization. SEM divulged important information regarding the structure of $MgCl_2$ and the influence of the diether donor. In the presence of the diether, controlled crystal growth gave large, well-defined $MgCl_2$ crystallites in which the formation of only 120^0 edge angles indicates the preference for the formation of a particular crystallite face. Long polymerizations clearly revealed polymer growth at the edges of the crystallites.

This approach is now being extended to an investigation of the role of different

Lewis bases (internal donors) and their interactions with $MgCl_2$, particularly in relation to their effect on the formation of (110) and (100) crystallite face(s) in the preparation of stereoselective Ziegler-Natta catalysts for propylene polymerization.

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