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The role of electron donors on lateral surfaces of $MgCl_2$-supported Ziegler–Natta catalysts: Observation by AFM and SEM

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ABSTRACT

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 silicon wafer, followed by crystal growth by Ostwald ripening to give well-defined $MgCl_2 \cdot \text{donor} \cdot n\text{EtOH}$ 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 $MgCl_2$. 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 $MgCl_2$. Subsequent treatment with $TiCl_4$ 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.

1. Introduction

Highly active $MgCl_2$-supported catalysts, containing $MgCl_2$, $TiCl_4$, and an "internal" electron donor, play a significant role in poly(propylene) (PP) production. In combination with a trialkylaluminum 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 $MgCl_2$-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 $TiCl_4$ in the catalyst. Giannini [2] indicated that on the lateral cleavage surfaces of $MgCl_2$, 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 $MgCl_2$. It has been proposed that bridged Ti_2Cl_8 species can coordinate to the (100) face of the $MgCl_2$ 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 $MgCl_2$ would therefore lead to the (100) face being prevailingly occupied by Ti_2Cl_8 dimers. However, recent mechanistic and modeling studies, in particular spectroscopic studies using FT-Raman [5,6], 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. Good performance in terms of stereospecificity can be reached only by preventing the displacement of the internal donor coordinated to $MgCl_2$. 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 AlR_3 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 $MgCl_2$.

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	Alkoxysilane
$MgCl_2/TiCl_4$/diether	AlR_3	

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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 alkoxysilane donor $RMe_2Si(OMe)$ was able to bind to both the (104) and the (110) edge surfaces, whereas a bidentate alkoxysilane, $RMeSi(OMe)_2$, 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, $MgCl_2{\cdot}n\mathrm{EtOH}$, 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 molecular sieves. The diether donor used was 9,9-bis(methoxymethyl)fluorene [16]. Diisobutyl phthalate ($\geqslant$98%) and ethyl benzoate ($\geqslant$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 $MgCl_2{\cdot}n\mathrm{EtOH}$ support and SiO_2/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 $MgCl_2$/donor$\cdot n$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 $MgCl_2$/diether$\cdot n$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 $MgCl_2$/donor$\cdot n$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 $MgCl_2{\cdot}n\mathrm{EtOH}$. 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

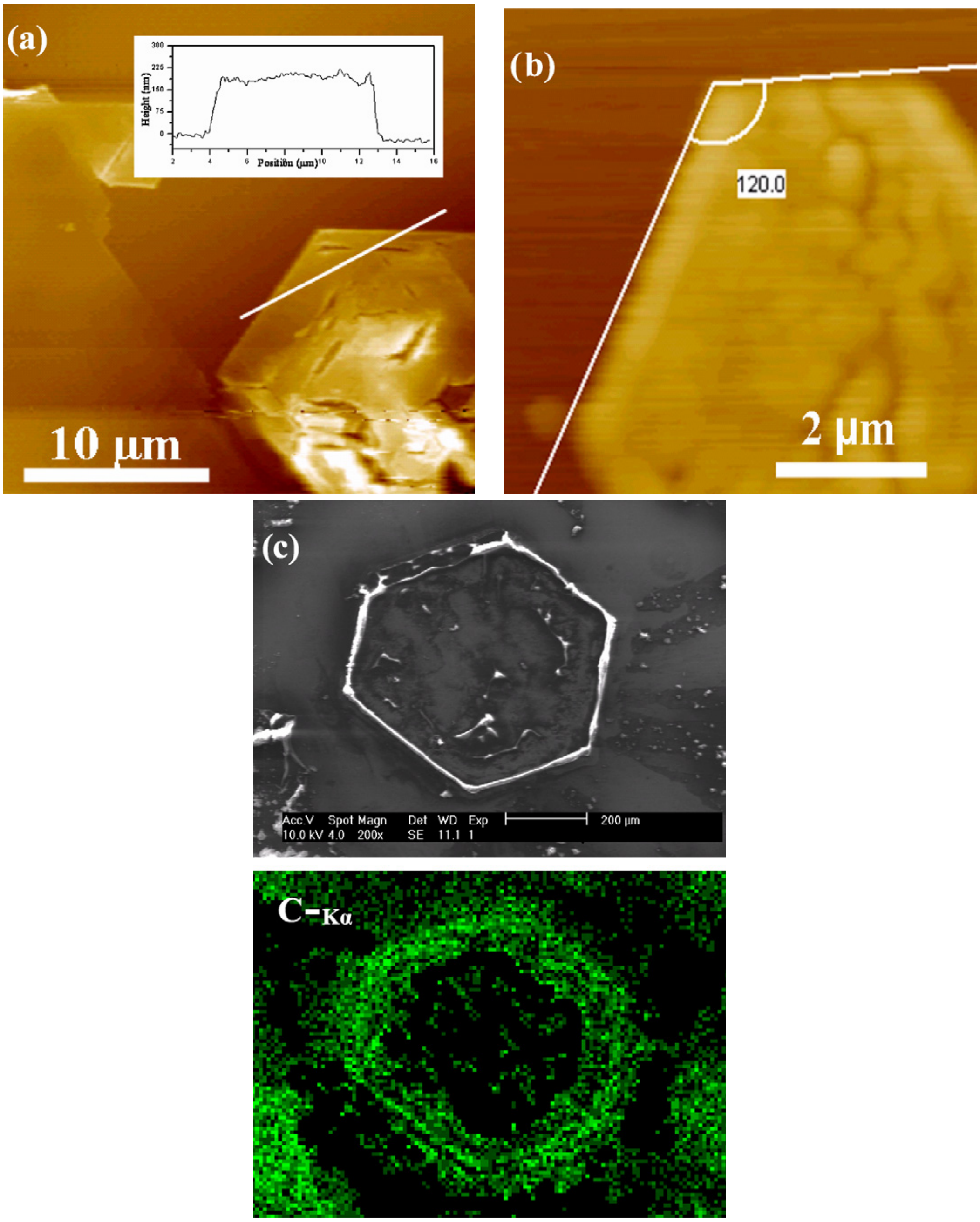

Fig. 1. (a) AFM image of $MgCl_2$·diether·*n*EtOH crystallite on a silicon wafer with the corresponding cross-sectional height scan (inserted image). (b) AFM image of $MgCl_2$·diether·*n*EtOH crystallite on a silicon wafer after treatment with $TiCl_4$ showing angle measurement (120°). (c) SEM image and SEM-EDX mapping of CK_α of poly(propylene) obtained after 16 h polymerization on a silicon wafer. Internal donor: 9,9-bis(methoxymethyl)fluorene.

Ziegler–Natta catalyst [17]. Spin-coating of a solution of magnesium chloride and a donor in ethanol onto a flat silicon wafer produces a solid layer which may be expected to consist of small particles of $MgCl_2$·donor·*n*EtOH. In order to convert this material to well-defined crystallites large enough to be characterized by AFM and SEM, the spin-coated layer was subjected to a process of Ostwald ripening. This process induced large changes in crystallite size and morphology. AFM images of the crystallites obtained are shown in Figs. 1a and 1b, which reveals the formation of micron-sized crystallites. Well-defined crystal faces and angles are apparent in these AFM images. In Fig. 1a, hexagonal structure is apparent. The corresponding cross-sectional height scan of the crystallite demonstrates a rather flat surface with a height profile of ±225 nm and with a roughness of ±25 nm. Fig. 1b represents an AFM image recorded after the Ostwald-ripened support was treated with $TiCl_4$. A sharp 120° edge angle is noticeable, indicating that the crystallites preserve their structure during the catalyst preparation. Fig. 1c represents a SEM image and SEM-EDX mapping of carbon after propylene polymerization was carried out for 16 h at ambient temperature. It is essential to mention that the SEM images presented in this work were taken after transport of the polymerized catalyst through air. While the original $MgCl_2$ crystal is destroyed, the poly(propylene) formed remains intact, creating an image of the distribution of polymerization activity on the model catalyst. A well-defined hexagonal crystal structure and 120° edge angles are evident in this image suggesting formation of only one crystallite face, i.e. either the (110) or the (104) face. In addition, the SEM-EDX mapping of the CK_α distribution reveals polymer formation on the corners and edges of the hexagonal crystallite. In contrast to the carbon mapping, AlK_α mapping (not shown) indi-

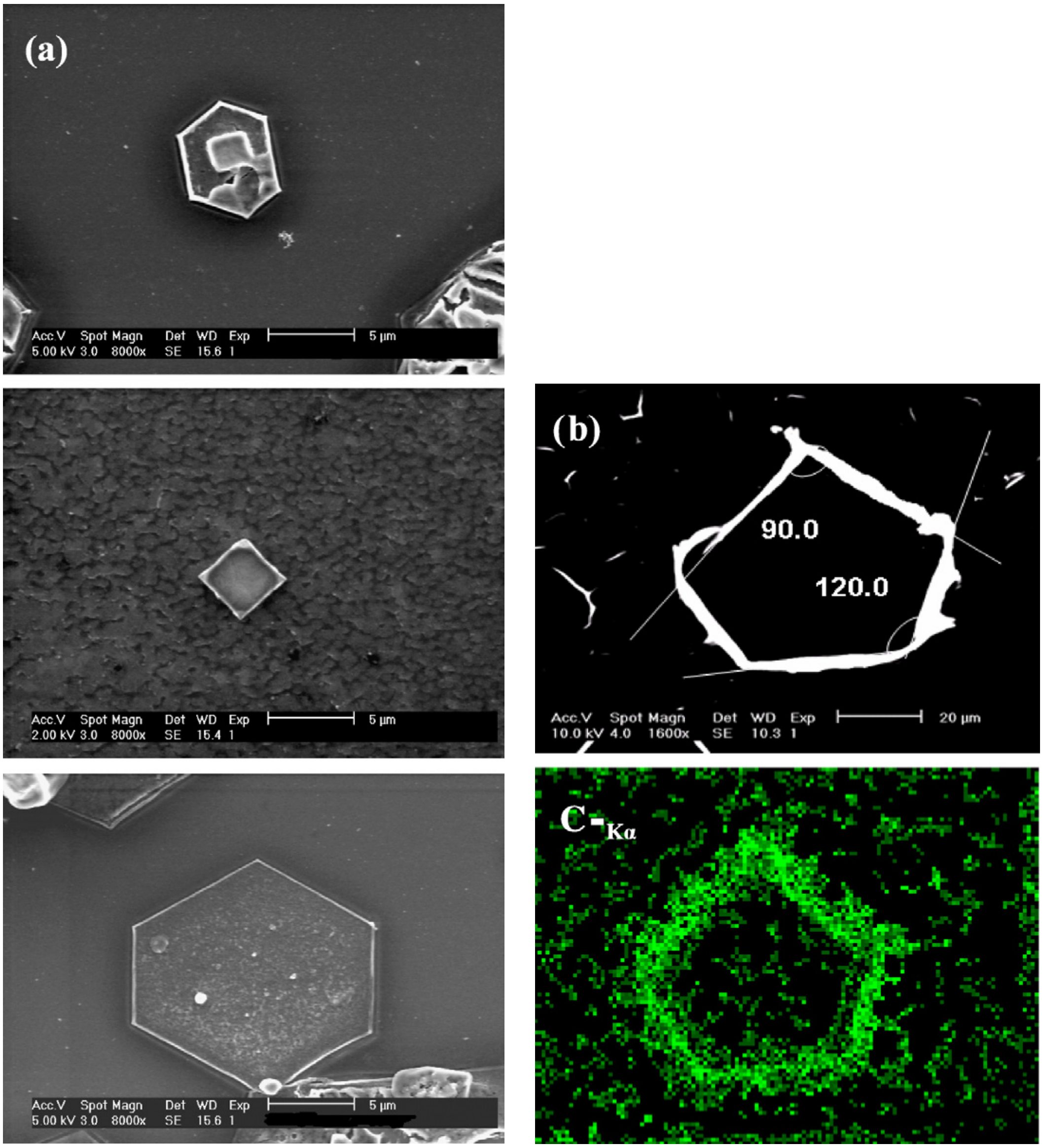

Fig. 2. (a) SEM images of poly(propylene) obtained after 2 h polymerization on a silicon wafer. Internal donor: diisobutyl phthalate. (b) SEM image and SEM-EDX mapping of CK_α of poly(propylene) obtained after 2 h polymerization on a silicon wafer. Internal donor: diisobutyl phthalate.

cated that aluminum, originating from the co-catalyst, is located all over the Si wafer. The crystallite in Fig. 1c is much larger than those shown in Figs. 1a and 1b, enabling easy morphological characterization by SEM as opposed to AFM. These results indicate that the Ostwald ripening procedure used for crystal growth results in a broad range of crystallite sizes, but the formation of hexagonal crystallites with 120° angles is independent of the crystallite size; the hexagonal crystallite morphology exemplified in Fig. 1 was consistently obtained in repeated experiments whenever the diether was present.

Replacing the diether by diisobutyl phthalate (DIBP) or ethyl benzoate (EB) has a profound effect on the morphology of the magnesium chloride crystals. SEM images taken after 2 h polymerization, with DIBP and ethyl benzoate as internal donor, reveal (Figs. 2a and 3a) again well-defined structures, but now rectangular as well as hexagonal crystallites are apparent. The controlled crystal growth to give well-defined $MgCl_2$ crystallites with a mixture of 120° and 90° edge angles indicates that both the (110) and (104) crystallite faces of magnesium chloride have been generated in the presence of DIBP and EB. Further investigation of this system also revealed the co-existence of 120° and 90° edge angles in a single crystallite, as shown in Figs. 2b and 3b. The additional SEM-EDX images of carbon indicate polymer growth on the edges and corners of the crystallites, although it is not possible to determine the relative amounts of polymer formed on each crystallite face. Aluminum mapping (not shown) revealed that in both systems the co-catalyst was located all over the Si wafer. The presence of 90° and 120° edge angles crystallites exemplified in Figs. 2 and 3 was consistently obtained in repeated experiments whenever the diester or monoester was present.

4. Discussion

The crystallization of magnesium chloride from a solution in ethanol gives hexagonal single crystals of the adduct $MgCl_2 \cdot 6EtOH$ [18]. In the present work, the formation of hexagonal crystallites with only 120° edge angles in the presence of the diether points to the exclusive formation of only one crystallite face, i.e. either the (110) or the (104) face. The preferential formation of the (110) face is most probable, taking into account the strong indications from modeling studies that the dominant coordination mode of diethers to $MgCl_2$ is via bidentate coordination on the (110) cut

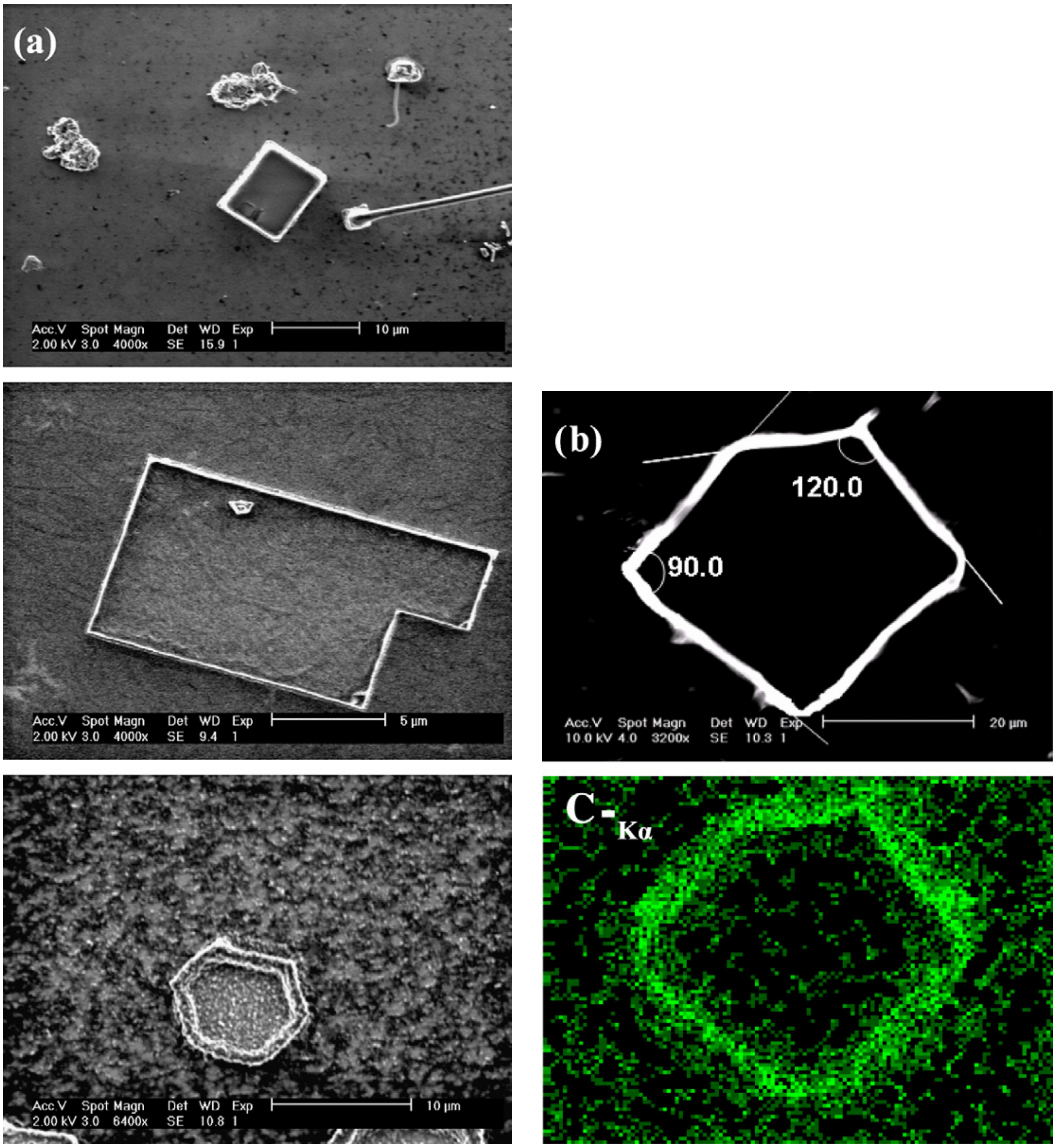

Fig. 3. (a) SEM images of poly(propylene) obtained after 2 h polymerization on a silicon wafer. Internal donor: ethyl benzoate. (b) SEM image and SEM-EDX mapping of CK_α of poly(propylene) obtained after 2 h polymerization on a silicon wafer. Internal donor: ethyl benzoate.

[19,20]. It has indeed been suggested [21] that the incorporation of a bidentate internal donor such as a 1,3-diether may lead to the preferential formation of the (110) face of $MgCl_2$ and that active Ti species are present on the same face, on account of the strong evidence for close interaction between electron donors and isospecific active species on the support surface [22–24]. It is well known that the use of a diether as internal donor gives polymers with relatively narrow molecular weight distribution, indicating a more uniform distribution of active species than is present in catalysts containing an ester as internal donor [1,21,25,26]. The present finding that $MgCl_2$ crystallites with exclusively 120° edge angles are formed in the presence of a diether indicates that the relatively uniform nature of the active species in this system may be due to the formation of a single crystallite face, most likely the (110) face [19,20].

Another feature of poly(propylene) catalysts of type $MgCl_2$/$TiCl_4$/diether is their particularly high activity, which can be around twice that obtained with catalysts containing a diester as internal donor. Interestingly, when a diether is used as external donor with a catalyst of type $MgCl_2$/$TiCl_4$/DIBP, the active species are very similar to those formed when the diether is used as internal donor [8,27,28]. However, the catalyst activity is lower. A possible explanation for this would be that, in catalyst preparation using an ester as internal donor, $MgCl_2$ crystallites containing both the (110) and the (104) edge faces are formed but that active species having high activity and stereospecificity are formed only on the (110) face. Recent density functional calculations by Taniike and Terano have indicated that, with ethyl benzoate, interaction between the donor and the Ti species takes place selectively on the (110) surface of the $MgCl_2$ support [29]. Correa et al. have described possible active species on the (110) lateral cut of $MgCl_2$, taking into account the preferential coordination of a diether on this surface, in contrast to a variety of possible modes of coordination of phthalates and succinates on $MgCl_2$ support surfaces [30]. These authors indicated also that the broader polydispersity (M_w/M_n) observed with a phthalate or succinate internal donor than with the diether-containing catalysts can be attributed to the variety of possible modes of coordination of esters on $MgCl_2$ support surfaces.

The present study provides strong evidence that the dependence of the distribution of active species in Ziegler–Natta catalysts for poly(propylene) on the nature of the internal donor is related to the ability of the donor to steer the formation of a particular $MgCl_2$ crystallite face during catalyst preparation. The results are as yet qualitative rather than quantitative, but indicate that a diether is effective in promoting the formation of the (110) surface, even though this surface has substantially higher energy than the (104) surface. It has been noted by Busico and co-workers that chemisorption of a donor on different surfaces may lower surface energies to different extents, thus changing their relative stabilities [10].

5. Conclusion

The characteristics of magnesium chloride supports generated in the synthesis of Ziegler–Natta catalysts are strongly dependent on the type of electron donor present in support and catalyst. Comparison of the effects of diether and ester donors in the controlled growth of $MgCl_2$ crystallites, following spin-coating of $MgCl_2 \cdot donor \cdot n EtOH$ from ethanol solution onto a flat silicon wafer, reveals that the presence of a diether leads to the formation of well-defined $MgCl_2$ crystallites in which the presence of only 120° edge angles indicates a strong preference for the formation of a particular crystallite face. In contrast, the use of a monoester or diester as internal donor generates crystallites with 120° and 90° edge angles, indicating the presence of both the (110) and the (104) edge surfaces of $MgCl_2$. Polymer growth takes place at the edges of the crystallites. The high activity and relatively uniform nature of the active species in catalysts of type $MgCl_2/TiCl_4$/diether is likely to be due to preferential formation of the (110) face of $MgCl_2$ when using a diether as internal donor in catalyst preparation. In further studies, we intend to extend the present AFM and SEM investigations and perform *in situ* TEM experiments to further characterize supports prepared in the presence of various internal donors, and to quantify the amount and tacticity of polymer formed on each crystallite face.

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