A Ziegler-type spherical cap model reveals early stage ethylene polymerization growth versus catalyst fragmentation relationships

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Polyolefin catalysts are characterized by their hierarchically complex nature, which complicates studies on the interplay between the catalyst and formed polymer phases. Here, the missing link in the morphology gap between planar model systems and industrially relevant spherical catalyst particles is introduced through the use of a spherical cap Ziegler-type catalyst model system for the polymerization of ethylene. More specifically, a moisture-stable LaOCl framework with enhanced imaging contrast has been designed to support the TiCl4 pre-active site, which could mimic the behaviour of the highly hygroscopic and industrially used MgCl2 framework. As a function of polymerization time, the fragmentation behaviour of the LaOCl framework changed from a mixture of the shrinking core (i.e., peeling off small polyethylene fragments at the surface) and continuous bisection (i.e., internal cleavage of the framework) into dominantly a continuous bisection model, which is linked to the evolution of the estimated polyethylene volume and the fraction of crystalline polyethylene formed. The combination of the spherical cap model system and the used advanced micro-spectroscopy toolbox, opens the route for high-throughput screening of catalyst functions with industrially relevant morphologies on the nano-scale.
mechanisms of Ziegler-type catalysts such as the nature of the exposed and unsaturated lattices on MgCl₂ that can chemisorb TiCl₄ and their relationship towards the formation of isotactic polypropylene. However, an alternative strategy is to simplify the hierarchically complex nature of these catalysts altogether through the design of planar model systems. These model systems have the additional advantage of being compatible with surface-sensitive spectroscopy and microscopy techniques, such as atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Somorjai and his group pioneered the field of using surface science techniques on planar model systems of Ziegler-type catalysts. In one of their early works, they found experimental evidence for the TiCl₄ activation mechanism as proposed theoretically by Adman and Cossee using an ultra-thin MgCl₂ film on a gold substrate. Siokou and Ntai switched towards the use of a facile spin-coating technique to produce a Ziegler-type planar model system based on tetrahydrofuran (THF) adducts with MgCl₂ and TiCl₄, which is in close analogue to the chemical activation routes of MgCl₂ used industrially. The effect of the type of internal donor on the stabilization of the unsaturated (110) and (104) lattices for a Ziegler-Natta planar model system was nicely studied by the group of Niemantsverdriet by growing well-defined crystals on a SiO₂/Si(100) substrate using a combined spin-coated and solvent vapour annealing approach.

For these conventional MgCl₂ based Ziegler-type catalyst model systems however, technical and experimental limitations are imposed due to the high moisture sensitivity of MgCl₂, which will lead to morphology changes under ambient conditions. Recently, Piovan et al., reported a chlorinated δ-Al₂O₃ support matrix instead of MgCl₂ to facilitate in-situ ethylene oligomerization at Al³⁺ sites for the production of a linear low-density polyethylene grade (LLDPE). The use of such non-conventional support matrices for Ziegler-type catalysis inspired us to design a model system for ethylene polymerization using a LaOCl support matrix due to two reasons. First of all, LaOCl provides strong interactions towards the formation of isotactic polypropylene. Secondly, exceptional moisture stability to facilitate ambient measuring conditions for the selected advanced micro-spectroscopy toolbox.

Whereas LaOCl has been reported as a promising catalyst material for the selective alkane activation, such as the conversion of methane to δ-MgCl₂, which resembles the δ-TiCl₃ phase, there is no hexagonal crystal structure. Additionally, other factors that explain the success story of MgCl₂ as a support matrix are the similar ionic radii of Mg²⁺ (∼0.72 Å) and Ti²⁺ (0.67 Å) and Ti⁴⁺ (∼0.61 Å) as well as the similar bond lengths of Mg-Cl and Ti-Cl (respectively, 2.4 Å and 2.3 Å). In the case of La³⁺ both a larger ionic radius (∼1.22 Å) and longer La-Cl bond length (∼2.4 Å) is observed. Both MgCl₂ and LaOCl are built up of layered structures that are platelets loosely bound together through ionic interactions. After grafting the TiCl₄ active site precursor on the LaOCl spherical caps followed by the activation with a triethylaluminium (TEAL) co-catalyst, ethylene polymerization under mild conditions, e.g., 2 bar ethylene, slurry-phase at room temperature, the polyethylene-LaOCl composite spherical caps are studied in detail using a toolbox consisting of both surface-sensitive (micro)-spectroscopic and conventional micro-spectroscopic techniques.

Both the surface-sensitive techniques, XPS and ToF-SIMS, and the bulk material probing Raman microscopy on the as-synthesized LaOCl spherical caps confirms the formation of the LaOCl phase as shown in the Supplementary Information sections 1 and 2. Additionally, XPS shows that after coordination of TiCl₄ to the LaOCl surface a minor amount of reduced Ti⁴⁺ is observed even before any contact with the reducing triethyaluminium (TEAL) co-catalyst. Although the majority of the Ti⁴⁺ species remain in the +4 oxidation state, it shows a possible similarity with the interaction and subsequent decomposition of CCl₄ on a LaOCl catalyst material through C₂Cl₂–C₃Cl intermediate species as reported by our group. The contribution of these minorly present reduced Ti⁴⁺ species to the overall catalytic activity after contact with a trialkylaluminium co-catalyst is under active spectroscopic investigation on a powdered-form LaOCl support matrix.

Introducing the micro-spectroscopy toolbox

In Fig. 2, an overview of the utilized micro-spectroscopy toolbox is given on a 20 min ethylene polymerized LaOCl spherical caps sample. Starting with ToF-SIMS, the composition of both the surface chemistry as well as the interior through depth profiling can be obtained. Here, a secondary electron image of an ethylene polymerized LaOCl spherical...
cap is shown together with the distribution of the negatively charged fragments of LaOCl⁻, TiOCl⁻ (due to exposure to moisture), and the polyethylene characteristic C–H stretches. AdditionalToF-SIMS results on a pristine LaOCl surface, different ethylene polymerization times and a HDPE reference film are given in the Supplementary Information section 3. With the vibrational micro-spectroscopy part of the toolbox, based on Raman microscopy and PiFM, the polyethylene phase is studied in-depth as shown in Figs. 2 and 3. Raman microscopy provides a time-efficient method to map the distribution of the -CH stretching vibrations in the region of 2700–3100 cm⁻¹ to visualize local thickness differences of the formed polyethylene phase within the spherical cap. However, even in the best-case scenario, the diffraction-limited spatial resolution of the Raman microscope setup utilized here would be on the order of 360 nm (see Eq. 1). On the other hand, with PiFM, IR spectra with the spatial resolution of the AFM tip’s apex (~20 nm) are obtained. This allows for the mapping and correlation of the -CH₂ bending vibrations of crystalline polyethylene at respectively 1461 cm⁻¹ (B₁u) and 1471 cm⁻¹ (B₂u) to the topological information obtained from the AFM part. Finally, FIB-SEM images provide strong Z-contrast between the low atomic weight polyethylene, the intermediate atomic weight Si(100) substrate and the high atomic weight LaOCl framework through the detection of backscattered electrons. Using both top-view and cross-sectional SEM images, the fragmentation of the LaOCl spherical cap as initiated by the induced stress of the polyethylene on the catalyst framework at respectively the spherical cap and the exterior volume can be observed. An in-depth study on this fragmentation behaviour of the LaOCl spherical caps at different ethylene polymerization times will be given around Fig. 4.

**In-Depth Study on the Formation of Polyethylene**

With the advanced micro-spectroscopy toolbox introduced for a 20 min ethylene polymerized LaOCl spherical cap, the formation of polyethylene will now be studied in-depth using the vibrational micro-spectroscopy part of this toolbox. To complement this 20 min ethylene polymerized sample, Raman microscopy and PiFM results of three additional ethylene polymerization times, namely 2, 5 and 60 min, are given in Fig. 3. The results on other polymerization times of respectively, 0 (pristine), 1 and 10 min are given in the Supplementary Information sections 2 and 4. In Fig. 3a, Raman microscopy results of the -CH stretch region at 2700–3100 cm⁻¹ are given to map the distribution and thickness fluctuations of the formed polyethylene. Starting at the 2 min ethylene polymerization sample, the formation of polyethylene can clearly be observed both at the centre and edges of the spherical cap. Interestingly, at the edges of the spherical cap the Raman signal intensity characteristic for polyethylene is higher than at the centre. Upon increasing the polymerization time towards 5, 20 and finally 60 min we observe two trends. The first is that of a more complete, denser coverage of the formed polyethylene over the spherical cap and the second is the increase of the overall intensity of the polyethylene phase indicating the formation of thicker polyethylene layers and thus increased polyethylene yields as a function of polymerization time (increase in the contrast of darker background versus intense polyethylene signals as function of polymerization time). The Raman maps are nicely complemented by the high spatial resolution PiFM maps in Fig. 3b, which shows that already at the early polymerization times we can observe well-defined and intertwined polyethylene fibres growing outwards of the LaOCl spherical caps and extending towards the Si(100) substrate background. For the 60 min polymerized sample, at the bottom left and therefore close to the centre or thickest point of the spherical cap, a LaOCl fragment can be observed to lay partially within and on top of the polyethylene fibres. The polyethylene layer here reaches a thickness of up to 5 microns as shown in Fig. S9, which is pushing the limits of the experimental setup. Additional topological images of the full spherical caps and zoomed-in PiFM maps of all polymerization times are given in Supplementary Information section 4, showing the presence of polyethylene fibres at all polymerization times as well as the increase in the overall polyethylene...
thickness and thus polyethylene yield as a function of polymerization time.

In Fig. 3c, the IR spectra obtained from PiFM are given for all the polymerization times studied. The signal-to-noise-ratio for the 1 and 2 min ethylene polymerization time are quite low, which could be explained either by the formation of the highly porous and thin polyethylene films at such low polymerization times or that the crystallinity of the polyethylene fibres is lower at these earlier polymerization times, leading to a higher contribution of an amorphous polyethylene phase. As the polymerization time increases, the clear doublet peaks of crystalline polyethylene appear after roughly 5 min of polymerization.

Using multivariate curve resolution (MCR), the contribution of the -CH₂ bend vibrations at 1461 cm⁻¹ and 1471 cm⁻¹ belonging to crystalline polyethylene in the orthorhombic phase and a broad amorphous band at 1463 cm⁻¹ as well as an interference component due to adsorption of water vapour were assessed⁴⁶,⁴⁷. The scores of this MCR, which can be thought of as the concentration of a spectral component in the sum spectrum, were subsequently used to calculate the fraction of crystalline components to the overall intensity of the 1400–1500 cm⁻¹ region (that is the two crystalline and one amorphous bands). This fraction as a function of ethylene polymerization time is shown in Fig. 3c. Initially, this fraction increases with polymerization time up to 10 min and then decreases and stabilizes for the 20 and 60 min samples. The increase of the fraction of crystalline bands as a function of polymerization time could be related to the polymerization rate where AFM and ToF-SIMS analysis in Figs. S8 and S11 show a decay in the increase of the estimated polyethylene on the external surface after roughly 2–5 min. This decrease of the polymerization rate, most likely due to internal mass transfer limitations within the LaOCl spherical caps, could then lead to a higher ratio of the rate of crystallization versus polymerization, since α-olefin polymerization is highly exothermic and can delay the crystallization of the formed polyolefin fibres. This would finally result in a higher fraction of crystalline components estimated with PiFM and subsequent MCR analysis with respect to the amorphous component. The decrease of the crystalline fractions for the 20 and 60 min polyethylene samples as compared to the 10 min polyethylene sample could be due to the increase of the chain length of the polyethylene phase as no chain-terminating reagent, such as H₂, is employed. The increased polyethylene chain length leads to a decrease in the crystallization rate due to the increased viscosity of these longer polyolefin chains⁴⁶. However, it should be emphasized here that no claims are made to the actual value of the crystallinity of the formed polyethylene phase, which is more conventionally assessed with bulk techniques such as differential scanning calorimetry requiring at least milligram quantities of polyethylene (DSC)⁴⁹.

**On the fragmentation behaviour of the spherical cap catalyst**

The vibrational microscopy part of the imaging toolbox confirmed the formation and evolution of the polyethylene crystallinity as a result of the ethylene polymerization reaction. Additionally, the formation of highly intertwined polyethylene fibres could be observed with the high spatial resolution PiFM maps, especially for the earliest polymerization times. To provide insights into the morphological evolution of the polyethylene phase as well as the fragmentation behaviour of the LaOCl support matrix, top-view and cross-sectional FIB-SEM is utilized.
spectra that give the -CH\textsubscript{2}- symmetric bending mode peaks of crystalline
polyethylene in an orthorhombic phase are shown after different polymerization times, averaged of 18 spectra measured on 9 different patterned catalysts per time. Multivariate curve resolution (MCR) analysis was performed to fit the individual spectra on 4 different spectral components. The fraction of the two crystalline components (1463 cm\textsuperscript{-1} and 1471 cm\textsuperscript{-1} bands) versus the single amorphous component (broad band at 1463 cm\textsuperscript{-1}) is plotted in terms of the mean and 95% CI per time, showing a steep increase in crystallinity up until 10 min, and then a saturation as the polymer layer is grown thicker and ordered to form HDPE-like PE, as seen in the spectral resemblance.

The observed fragmentation behaviour of these spherical caps consists of three stages as drawn schematically in Fig. S17. In the first stage, roughly 1 to 5 min of ethylene polymerization, the macroporous and surface-cracked LaOCl spherical cap comes in contact with ethylene that is transformed into polyethylene. Two different polymerization phenomena are observed in this first stage depending on the location within the spherical cap based on Figs. 4 and S19. Namely, (i) around the centre of the spherical cap, the first polyethylene fibres are extruded out of the surface exposed cracks and locally start to peel off the LaOCl framework, which becomes infused with the expanding polyethylene fibres. This peeling of small catalyst fragments belongs to the shrinking core fragmentation model and can clearly be observed in Fig. S19 for the zoom-ins on the 1 and 2 min polymerized samples (see Fig. S16). (ii) The formation of polyethylene within the internal macroporous cavities that leads to the rapid filling of such cavities. At the outer rim of the spherical caps this cavity filling is observed to lead to a significant degree of internal catalyst fragmentation already at this first stage. This type of catalyst fragmentation as described by the internal cleavage of the framework into successively smaller fragments belongs to the continuous bisection fragmentation model\textsuperscript{5}. A visualization of the shrinking core and continuous bisection fragmentation models is given in Fig. S16. The second stage, roughly 10 to 20 min of ethylene polymerization, expands on the first phase through the steady growth of both formed polyethylene phenomena observed. That is, the porous polyethylene network formed due to the extrusion of polyethylene fibres from the exposed surface cracks increases both in total surface coverage as well as thickness and the thicker polyethylene regions observed at the outer rim, which cause a heavy local degree of framework fragmentation, increase further in thickness. Additionally, these thicker spheroidal regions, leading to a high degree of internal catalyst fragmentation, start to appear now also around the centre of the spherical cap as the build-up of stress exerted on the locally thicker LaOCl framework region has now surpassed the required threshold. The presence of these spheroidal regions that contain a thicker polyethylene phase were also observed earlier with the Raman microscopy maps in Figs. 3 and S5 as the regions with the higher signal intensity of the polyethylene characteristic -CH stretch vibrations. Finally, in the third stage, at 60 min of ethylene polymerization, the polymerization activity has been sufficiently high to cause a full disintegration of the original spherical cap morphology in both small and large LaOCl fragments, which however still show additional internal crack lines, dispersed uniformly throughout the formed polymer stage. The presence of these small and large LaOCl fragments with internal cleavage lines that are homogeneously dispersed throughout the formed polyethylene phase show that the continuous bisection fragmentation model has become the dominant fragmentation pathway for prolonged polymerization times.

Finally, to validate the LaOCl support matrix introduced in this study, a reference MgO/MgCl\textsubscript{2} core-shell cap model system was
In this work, a spherical cap model system has been introduced to bridge the gap between conventional planar model catalyst systems and the industrially used spherical catalyst particles in the field of α-olefin polymerization. Additionally, for this model system, LaOCl was chosen as a support matrix instead of the conventional MgCl2 support matrix to support the TiCl4 pre-active site. This provided both enhanced imaging contrast due to the high atomic weight of the lanthanum-based matrix and excellent moisture stability to enable the use of advanced micro-spectroscopy techniques under ambient conditions in contrast to the low atomic weight and highly hygroscopic MgCl2. X-ray photo-electron spectroscopy (XPS) gave evidence for the coordination of Ti4+ and even a minor presence of Ti3+ species on the LaOCl surface before contact with the triethylaluminium co-catalyst. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and Raman microscopy confirmed the LaOCl chemical phase on the spherical cap model as well as the formation of polyethylene at all polymerization times studied. Raman microscopy, photo-induced force microscopy (PiFM) and cross-sectional scanning electron microscopy (SEM) show the presence of two morphologically distinct polyethylene phases formed with (i) discrete and thicker polyethylene regions starting to be formed at the outer rim of the spherical cap at early polymerization times that gradually start to cover also the centre of the spherical caps and (ii) a network of highly intertwined polyethylene fibres distributed more uniformly over the spherical cap. Additionally, SEM shows that the polyethylene fibres are extruded out of crack lines already present on the pristine catalyst’s surface, which are subsequently expanding further due to the stress of the polymer induced on the framework. These extruded polyethylene fibres peel off small LaOCl fragments from the surface. At the outer rim of the spherical caps, large LaOCl fragments are lifted up from the framework due to the polymerization of ethylene within the LaOCl porous framework and confirms the observations made with Raman microscopy and PiFM of locally thicker and
spheroidal polyethylene regions. These findings show that both limiting modes of fragmentation, namely the shrinking core (peeling off small fragments at the surface) and continuous bisection (internal cleavage of the framework) are occurring simultaneously throughout the polymerization process at early polymerization times. However, at 60 min ethylene polymerization, a full disintegration of the spherical cap morphology is observed according to a dominating continuous bisection fragmentation model. A reference MgO/MgCl₂ cap system, which was observed to be highly susceptible to morphology changes upon exposure to moisture and possesses limited Z-contrast, showed a higher ethylene polymerization activity than the LaOCl framework but a similar dominant fragmentation pathway, namely that of continuous bisection. The use of this industrially relevant spherical cap model system can be expanded further for the high-throughput testing of support matrix formulations (both conventional and unconventional) in the field of α-olefin polymerization. These options include the use of highly tuneable and controllable deposition techniques such as inkjet printing as well as table-top SEM, Raman microscopy and scanning probe microscopy (AFM and PFM) apparatus capable of fitting inside a glovebox or through the use of transfer vessels and inert measuring chambers. Furthermore, semi-quantification of the Ti content through the use of additional highly sensitive imaging techniques such as µ-XRF or electron probe microanalysis could open the route to provide activity estimates of each individual spherical cap regarding ethylene polymerization. Finally, through modifying the polymerization reactor with high pressure and temperature capabilities as well as implementing mechanical overhead stirring to limit external mass transfer limitations combined with rapid quench methods, industrially relevant polymerization conditions could be mimicked.

Methods

Material synthesis

B-doped Si(100) wafers with a thickness of 525 µm and resistivity of 0.005 Ohm-cm were purchased from Siegert Wafer. After cutting the wafers in suitable sizes (~5 × 5 mm² in size) with a diamond knife, a procedure for the grafting of the self-assembled monolayer and subsequent photo-patterning was followed as reported in literature. First, the wafer pieces were cleaned with a 1:1 volumetric ratio of demineralized water, ethanol and acetone using an ultrasonicator for 15 min to remove surface contaminants. This step was then repeated in demineralized water for again 15 min. Then, the wafer pieces were placed in a beaker glass with a 3:1 volumetric ratio of demineralized water, ammonium hydroxide (28–32 wt% in H₂O, Sigma-Aldrich) and hydrogen peroxide (30 wt%, Sigma-Aldrich) and placed on a hotplate at 65 °C for 30 min. In this step, the native oxide surface layer on the Si(100) substrate is partially etched away and converted into surface hydroxyl groups. Afterwards, the wafers were first placed in a beaker of room-temperature demineralized water to quench this etching step and then heated to around 95 °C in demineralized water to remove any surface absorbed ammonium species for an additional 30 min. The wafer pieces are blown dry with a N₂ line and then placed in an oven at 120 °C for 1 h. This is followed by the transfer of the wafer pieces to a glovebox operating at <1 ppm O₂ and then placed in an oven at 120 °C for 1 h. Spinning was performed at 3000 rpm for 30 s with an injection volume of 10 µL on the wafer surface and a loading time of 5 s. After the spin-coating, the wafer pieces were transferred into a quartz boat that was subsequently placed inside a tube oven under dry N₂ flow of 200 mL/min. The heat treatment method consisted of three steps. First with a ramp of 2 °C/min to a temperature of 250 °C and dwell time of 4 h, followed by heating up to 600 °C with the same ramp and staying for an additional 4 h. Finally, the oven was cooled down 200 °C where it remained until the wafers were brought at this temperature into the glovebox. In the case of the MgO/MgCl₂ reference sample, the same spin-coating and calcination method was used, including the direct transfer of the MgO intermediate chemical phase (from the calcination step at 200 °C) into the glovebox. For the spin-coating step, a 20 mM magnesium nitrate hexahydrate (99%, Sigma-Aldrich) solution in ethanol was prepared. The grafting of the TiCl₄ pre-active site onto the LaOCl spherical cap system has to be performed under stringent controls (<1 ppm O₂/H₂O) to prevent decomposition of TiCl₄ and was done inside a glovebox. In a 20 mL glass vial, a 30 vol% solution of TiCl₄ (99.9%, Sigma-Aldrich) in anhydrous heptane (99.9% stored over 4 Å molecular sieves, Sigma-Aldrich) was prepared to which the wafer pieces were added. The vial was then closed, wrapped in aluminium foil for better heat transfer, and put on a hotplate at 95 °C for 1 h. Afterwards, the vial was cooled down to room temperature naturally, after which the wafer pieces were transferred sequentially through three glass vials filled with pure heptane to remove excess TiCl₄. In the last step of the three washing vials, the wafers were kept for 30 min until they were transferred to a final fourth vial filled with heptane where they were kept for storage until commencing ethylene polymerization. In the case of the MgO/MgCl₂ reference sample, the chlorination of the MgO spherical caps was performed based on the work of Chamingkwan et al. However, instead of using pure TiCl₄ under refluxing conditions, we chose to use the 30 vol% solution of TiCl₄ in heptane at 95 °C for 1 h as performed also for the grafting of TiCl₄ on LaOCl. Afterwards, the same washing steps were performed as for the LaOCl spherical cap samples and were kept in a vial filled with heptane for storage until commencing ethylene polymerization.

Material testing

A custom-made low-pressure polymerization set-up was built to run inside the glovebox. This set-up allows us to either evacuate a cylindrical glass reactor with an internal volume of roughly 100 mL using an external vacuum pump or feed ethylene (4.5 N purity, Linde) at a pressure of 2 bar. The reactor was filled with a 10 mL anhydrous heptane solution containing 1 mg/mL triethylaluminium (98%, Sigma-Aldrich). The reactor was then slowly evacuated without stirring to remove the N₂ atmosphere followed by feeding the ethylene at 2 bar until the solution became saturated. Meanwhile, the wafer pieces that now have the TiCl₄ pre-active site grafted on the LaOCl surface were still stored in heptane. Two wafer pieces per polymerization time were then taken out and dried for 1 min under a N₂ atmosphere. After saturating the solvent with ethylene, the reactor was slowly evacuated to atmospheric pressure, opened and quickly the two wafer pieces were placed inside the reactor followed by closing the reactor again. The reactor was then repressurized with ethylene in the absence of stirring and at this moment the timing of the polymerization reaction was commenced. The steps from placing the wafers in the...
ethylenic saturated solution to closing the reactor and depressurizing typically took about 10 s. Quenching of the reaction was performed by quickly evacuating the reactor after the desired time, filling the reactor with N₂, opening the reactor and placing the wafer pieces in a separate vial containing several mL of pure heptane. These vials were then taken out of the glovebox and placed inside an ultrasonicator for 90 s followed by drying under a mild N₂ flow. The ultrasonicator step was found to be necessary to remove what would otherwise form a thick film originating from the hydrolysis of the co-catalyst after exposure to air. Afterwards, the polymerized wafers were dried overnight in a 60 °C oven and stored in a container labelled with the polymerization time.

Focused ion beam-scanning electron microscopy
Focused ion beam scanning electron microscopy (FIB-SEM) images were collected on a FEI Helios NanoLab G3 UC scanning electron microscopy. The wafers of interest were placed on aluminium SEM stubs using a conductive carbon tape on the back-side of the wafer. For SEM images, the accelerating voltage was set to 2 kV and the current to 0.10 nA and the backscattered electron images were collected with a through-lens-detector to take full advantage of the strong Z-contrast between LaOCl, the formed polyethylene and the Si(100) background. EDX elemental mapping was performed with a silicon drift detector (SDD) (X-MAX from Oxford Instruments). Prior to the milling of the region of interest with the focused ion beam a 3 µm thick Pt layer was deposited on top of the region of interest. The focus ion beam accelerating voltage was set at 30 kV and the current for both milling and cleaning at 0.43 nA. The milling was performed to create a trench perpendicularly to the surface and roughly at the centre of a spherical cap. After the milling step, the cross-section was cleaned with Ga ions before collecting the backscattered electron images.

Photo-induced force microscopy
Photo-induced force microscopy (PiFM) micrographs, intensity maps and spectra were collected on a Molecular Vista Vistascope microscope equipped with a block engineering tunable quantum cascade laser (QCL), having a 1965–2700 cm⁻¹ range. Gold coated tips (P = 100–130 N/m, resonance frequency >320 kHz) were used to obtain micrographs of the patterns of interest in semi-contact mode. Then, either the same ROI was scanned subsequently while changing the laser wavelength to 1471, 1461 and 1600 cm⁻¹ to collect individual intensity maps, or the tip was brought to a position of choice and a full spectrum was recorded with 1 cm⁻¹ resolution, 200 averages. The obtained height micrographs were post-processed in Gwyddion 55. A plane background was subtracted using a 2 pixel mean filter. To obtain a representative PiF spectrum per PE time, 9 different patterns per time and 30 accumulations. Background corrections were performed by quickly evacuating the reactor after the desired time, filling the reactor with N₂, opening the reactor and placing the wafer pieces in a separate vial containing several mL of pure heptane. These vials were then taken out of the glovebox and placed inside an ultrasonicator for 90 s followed by drying under a mild N₂ flow. The ultrasonicator step was found to be necessary to remove what would otherwise form a thick film originating from the hydrolysis of the co-catalyst after exposure to air. Afterwards, the polymerized wafers were dried overnight in a 60 °C oven and stored in a container labelled with the polymerization time.

FRACTION OF CRYSTALLINE COMPONENT

The fraction of the crystalline components (1461 cm⁻¹ and 1471 cm⁻¹) to that of the single amorphous component (1463 cm⁻¹) was calculated as shown in Eq. 1.

\[
\text{Fraction of crystalline components} = \frac{\text{sum of crystalline polyethylene component (#1+#4) scores}}{\text{sum of all polyethylene component (#1+#3+#4) scores}} \times 100\%
\] (1)

Atomic force microscopy
Atomic force microscopy (AFM) was recorded on a Bruker MultiMode 8 with J Scanner in non-contact ScanAsyst HR mode, using silicon nitride ScanAsyst HR tips (F = 0.4 N/m, frequency ~130 kHz). Post polymerization time, 6 different patterned catalysts were measured (Fig. S9). The data were post-treated as explained before for the PiFM maps. Furthermore, \(x\) and \(y\) cross-sections were then plotted through the middle-point of the catalyst caps, and the resulting profiles were fitted using a power function on the exposed uncovered catalyst cap (Fig. S10). Then, the height and cap-base diameter, or chord length, were measured to obtain the catalyst volume, which could be subtracted from the total measured volume (obtained using Gwyddions “Statistics” function) to yield the net polymer volume. More information can be found in the Supplementary Information. In the case of the MgO/MgCl₂ reference sample, the initial scan was performed with an identical model (and experimental approach) installed inside a glovebox operating at <1 ppm O₂ and H₂O. The location of the pattern was determined with optical microscopy, and then the sample was transferred to the AFM outside the glovebox. The moment the sample left the glovebox was denoted as “0 min”. Further AFM scanning and post-treatment was done as described before.

Raman microscopy
Raman spectra were collected with the XploRA™ PLUS Raman Spectrometer – Confocal Raman Microscope from Horiba Scientific. At all times a 532 nm excitation laser and 100x objective with 0.9 NA was used together with a 1200 mm⁻¹ grating and slit and hole sizes of respectively 200 µm and 500 µm. Knowing the NA of the objective and the wavelength of the laser, it is possible to calculate the diffraction limited spatial resolution according to Eq. 2, which would be ~360 nm for a λ = 532 nm and NA = 0.9⁹.

\[
\text{Spatial resolution} = \frac{0.61 \times \lambda}{NA}
\] (2)

To collect high resolution maps, a laser power of 25% maximum (15.55 mW) was used with a 30 ms dwell time, 1 accumulation per spectrum, a step size of 0.25 µm and a scan range of 2700–3100 cm⁻¹. To collect full-range, single point spectra, a laser power of 10% maximum (6.81 mW) was used with a 500 ms dwell time and 30 accumulations. Background corrections were performed within the Fityk software. No smoothing function was applied on the Raman spectra.

Time-of-flight secondary ion mass spectrometry
Time-of-flight secondary ion mass spectrometry measurements (ToF-SIMS) were carried out with a M6 Hybrid SIMS (IONTOF GmbH, Münster, Germany). The machine is equipped with a 30 keV Bi nanoprobe primary ion gun, low energetic (2 kV) Cs and EI gas sputter guns as well as a 20 keV Ar⁺(O₂)x gas cluster source. The samples were mounted with a double-sided copper tape on an electrical insulating glass slide.

Depth profiles were carried out with 30 keV Bi⁺ primary ions in non-bunched mode (aperture 200 µm) in delayed extraction mode with topography option at negative polarity. The Bi⁺
primary ion current was about 0.18 pA at 100 µs cycle time. The low energetic electron flood gun was used for charge compensation. Sputtering was done with a 10 keV Ar2000+ sputter beam (I ≃ 8 nA). Areas of 175 × 175 µm were probed in non-interlaced mode, with 512 × 512 pixels. The raster size of the sputter gun was 300 × 300 µm² centred to the analysis area. For data evaluation Surface Lab 7.2 (ION-TOF GmbH, Münster, Germany) was used. Mass calibration was carried out with the signals C, OH, C₂, Cl⁻, C₃H₅⁻, C₂H₅⁻, and LaOCl⁻. Calibration and comparison to literature HDPE ToF-SIMS spectra was performed with respect to the work by Kern et al.³⁷.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI5000 Versa Probe II system from Physical Electronics. The X-ray source was monochromatic Al Kα radiation (1486.6 eV). The pass energy for detailed spectra in the analyzer was 23.50 eV. Data evaluation was performed with CasaXPS (version 2.3.22, Casa Software Ltd.). Energy calibration was performed based on the signal of the adventitious carbon at 284.8 eV. The following three bulk reference La powders were measured: La₂O₃ (99.9%, anhydrous powder, Sigma-Aldrich), LaCl₃ (99.9%, anhydrous powder, Sigma-Aldrich), and LaOCl (synthesized as described by Peringer et al.³⁵). The XPS samples measured are based on the synthesis of LaOCl spherical caps with a 20 mM LaCl₃ -7 H₂O in ethanol solution as described earlier. These samples were measured as both pristine and after reaction with TiCl₄ at 95°C ex-situ. The in a N₂ glovebox prepared samples were stored in heptane and transported in a sealed, steel vacuum tube to an Ar-filled glovebox. There they were opened, dried under Ar atmosphere and transferred into the XPS system using a transfer vessel under Ar atmosphere.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

K.W.B., L.D.B.M., and B.M.W. envisioned the research and required project strategy. B.M.W. supervised the project. K.W.B. and L.D.B.M. wrote the initial manuscript. K.W.B. synthesized the LaOCl spherical cap model system and performed the polymerization reactions. Y.L. developed the methodology for the MgO/MgCl2 spherical cap model system after which Y.L. and L.D.B.M. synthesized the MgO/MgCl2 spherical cap samples. J.M.D. performed the polymerization reactions on the MgO/MgCl2 spherical cap samples. F.W. performed the multivariate curve resolution analysis and pre-processing of the PiFM data. N.N. performed the FIB-SEM-EDX experiments. M.R. and K.W.B. performed the ToF-SIMS experiments and M.R. and L.D.B.M. the subsequent analysis. F.W. performed the XPS experiments and the subsequent analysis. B.J.P.T. helped conceive the concept of LaOCl as a support matrix for Ziegler-type catalysis. B.M.W. revised the paper with contributions from all the co-authors.

Competing interests

The authors declare no competing interests.
