Supporting information

Heterogeneity in the Fragmentation of Ziegler Catalyst Particles during Ethylene Polymerization Quantified by X-ray Nano-Tomography

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1. Synthesis of the Ziegler Catalyst

A Ziegler catalyst, industrially relevant for the production of high molecular weight and high-density polyethylene without the addition of co-monomers was synthesized in accordance with the description in patent WO2009112254 [1]. The as-synthesized catalyst formulation resembles that of a typical MgCl₂/TiCl₄ Ziegler-type catalyst with a Ti weight loading of 4% obtained from Inductively Coupled Plasma- Atom Emission Spectroscopy (ICP-AES). The median particle size ($D_{50}$) and particle size distribution (span, defined as $\frac{D_{90} - D_{10}}{D_{50}}$) using Static Laser Scattering (SLS) were obtained using a Mastersizer 3000 laser diffraction particle size analyzer instrument. The $D_{10,50,90}$ values of the pristine catalyst are respectively 2.23, 3.64 and 6.01 µm giving a span of 1.04. Scanning electron microscopy (SEM) images of the pristine catalyst, transferred under inert conditions using a transfer module from Kammrath & Weiss, to a ThermoFischer FEI Versa 3D FEG SEM were obtained at a 2 kV accelerating voltage and are shown in Figure S1. Based on SEM, the pristine catalyst particles are observed to be elongated. N₂ physisorption on a typical batch of this Ziegler catalyst shows a BET surface area of 6.3 m²/g and a pore volume of 0.026 cm³/g. Only mesoporosity is observed for the catalyst with a pore size distribution mainly between 20 to 50 nm.

![Figure S1](image_url)  
**Figure S1** Scanning electron microscopy (SEM) images of the Ziegler catalyst used. The catalyst particles are observed to have a cauli-flower type of shape with a rough surface and cracks can be observed on the external surface, likely due to the agglomeration of smaller sub-units. A majority of the catalyst particles seems to be slightly elongated.
2. **Slurry-phase Ethylene Polymerization**

Due to the high sensitivity of the as-synthesized Ziegler catalyst to moisture and oxygen all further procedures were performed inside a glovebox operating under inert conditions of N\textsubscript{2} with <0.3 ppm H\textsubscript{2}O and <1 ppm O\textsubscript{2}. A low-pressure, room-temperature polymerization set-up was designed to run from inside the glovebox, with a schematic drawing given in Figure S2. A cylindrical glass reactor of circa 100 mL internal volume with a single inlet can be either set under vacuo to remove the gas atmosphere inside the reactor or be filled with ethylene at a set pressure of 1.2 barg. A typical polymerization reaction was performed as follows. First, 10 mL of anhydrous (99.9% purity, dried and stored over 3Å molecular sieves, Across Organics) heptane was introduced in the open glass reactor equipped with a magnetic stirring bar. A 500 µL solution of triethylaluminium co-catalyst (1M in heptane, Sigma-Aldrich) was then added whilst stirring at 400 rpm with a ratio with regards to the catalyst of [Al]/[Ti]= 72. The co-catalyst serves two purposes here, to further purify the diluent as well as the monomer gas-feed and to activate the Ziegler pre-catalyst. Meanwhile the catalyst that was kept in a hexane slurry was dried at room temperature inside the glovebox after which 50 mg was added to the diluent mixture in the reactor whilst stirring at 400 rpm. The reactor chamber was then closed and the evacuation/feed tubing attached. The reactor was first evacuated slowly to several tens of mbar pressure to remove the N\textsubscript{2} atmosphere after which the ethylene (3.5N purity, Linde) was fed to the reactor. During the entire duration of the polymerization reaction the gas-feed was kept open as to ensure a constant pressure of ethylene. After five minutes of polymerization, the ethylene feed was quickly removed by switching the reactor to the vacuum pump followed by introducing N\textsubscript{2}. The slurry was then filter dried inside the glovebox using the same vacuum pump set-up and washed successively three times with heptane and three times with pentane. Afterwards, the powder was dried for 60 minutes at room temperature followed by drying at 80 °C overnight on a hotplate inside the glovebox. The next day, the resulting dried polymer powder was weighed and gave a yield of 3.4 g HDPE / g catalyst after which it was stored until further use in a glass vial in the glovebox. The reactor set-up was designed for its simplicity in use inside a glovebox, however it should be noted that a model reactor for low polymer yields such as designed by the group of McKenna et al., would allow industrially relevant polymerization conditions whilst having high control over the polymer yield [2-5].

![Figure S2 Schematic representation of the lab-based model reactor for ethylene polymerization under mild conditions (pressure up to 1.6barg and room temperature)](image-url)
The polymer yield can also be estimated based on the median of the particle size distribution, \( D_{50} \), as shown in Equation (Eq.) S1:

\[
D_{50} - \text{polymer} = D_{50} - \text{catalyst} \cdot R_f \cdot \sqrt[3]{PY + 1} \quad \text{[Eq. S1]}
\]

Here \( D_{50}\text{-polymer} \) and \( D_{50}\text{-catalyst} \) are the \( D_{50} \) values of respectively the obtained polymer particles and the pristine catalyst used. \( R_f \) is a constant, which is assumed to be 1, and relates to the physical nature of the polymer and catalyst particles and that one catalyst particle is converted into one polymer particle. The polymer yield, \( PY \), gives the yield of polymer in terms of g polymer/g catalyst and can be deduced from Eq. S1 if one knows the \( D_{50} \) values of polymer and catalyst [6].

The particle size distribution (\( D_{10,50,90} \) and span) of the product was measured with SLS. The SLS results on these composite polymer-catalyst particles gave a \( D_{50} \) value starting at 371 \( \mu m \) that would decrease to 172 \( \mu m \) during 20 consecutive runs. The decrease in \( D_{50} \) based on the run-time is due to the constant mechanical stirring inside the SLS machine, which therefore indicates that the HDPE-Ziegler catalyst composite particles are highly agglomerated and break up due to the induced mechanical forces. SLS is able to measure such agglomerations since the working principle of SLS is based on the scattering of the laser light induced by any objects through its path towards the detector.

To confirm this agglomeration, SEM analysis was also performed of the polymerized catalyst sample and is shown below in Figure S3. Clearly HDPE fibers can be observed bridging multiple particles together in the right side of Figure S3. Whereas this catalyst yielded agglomerations at low yields, at industrially relevant yields on the order of several kg HDPE/g catalyst spherical and isolated HDPE particles are obtained. This indicates that at some point during the polymerization process, the mechanical forces induced by the stirring in addition to the ever-increasing diameter of the particles seem to overcome the strength of the fibers bridging two or more particles together and cause a deagglomeration process.

**Figure S3** Scanning electron microscopy (SEM) images of the ethylene polymerized Ziegler catalyst. The agglomeration of the composite polymer-catalyst particles is evident in the top left and bottom left images. Furthermore, the zoom-in SEM image in the right shows the presence of polymer fibrils below 100 nm thickness bridging particles together and is likely the reason of the agglomeration of the composite particles. Furthermore, the zoom-in shows the roughness of the particle surface is maintained.
Since, the $D_{50}$ of the composite polymer-catalyst particles from SLS are unreliable due to the strong agglomeration, the theoretical $D_{50}$ value was calculated based on Eq. S1. Here the polymer yield of 3.4 g HDPE / g cat was used, which was found simply by weighing the final polymer product and correcting for the amount of catalyst injected in the reactor. With the $D_{50\text{-catalyst}}$ value of 3.6 µm, that was found reliably with SLS for the pristine catalyst, the $D_{50\text{-polymer}}$ value is estimated to be 5.9 µm.

3. Loading of Sample in Polyimide Capillary

The sample loading inside a polyimide capillary was similar to that performed in our previous work and all actions were performed inside a N$_2$-filled glovebox operating at <0.3 ppm H$_2$O and <1 ppm O$_2$ unless otherwise stated [7]. Polyimide capillaries obtained from MicroLumen with an inside diameter of 120 µm and wall thickness of 10 µm were used. To load the agglomerated powder, which looks like small flakes, the capillary was gently inserted into a flake and turned up-side down so that the composite powder is now at the top of the capillary. The capillary is then mildly agitated by tapping it gently from the outside with a tweezer so that the agglomerated particles drop towards the center of the capillary. Care was taken not to squeeze the center of the capillary or hit the agglomerated particles directly with the tweezer as this could cause any unwanted morphological changes to the sample unrelated to the actual polymerization process. Finally, a two-component, low-outgassing and near-hermetic sealing epoxy from Epotek©, product label H74, was used to seal the two ends of the capillary. The epoxy had to be cured at 80 °C for 30 minutes to ensure the desired sealing effect. This was performed by placing the capillaries on a hotplate. To make sure the capillaries don’t get stuck on a hotplate, small aluminium foil pieces were attached to the ends of each tubing where the epoxy was applied. Transport from the glovebox environment to the synchrotron beamline was performed by placing the loaded capillaries inside glass vials sealed with Teflon tape and placing them in steel vacuum tubes fitted with Viton O-rings and a closing ring.

4. Synchrotron Correlated X-ray Ptychography and Fluorescence Microscopy Set-up

The correlated ptychography X-ray computed tomography (PXCT) and X-ray fluorescence (XRF) tomography experiment was performed at the Hard X-ray Micro/Nano-Probe beamline, P06, at the PETRA III synchrotron facility, DESY. The PXCT raw data was collected using an Eiger X 4M hybrid pixel detector (Dectris Ltd.). Two SII Vortex EM Si-drift detectors (internally collimated to a 50 mm$^2$ area) were used to collect the Ti XRF data-set. The field-of-view (FOV) of 120x20 µm (H x V) was raster-scanned with a coherent and monochromatic X-ray beam focused down to 170 x 160 nm (H x V) at 12 keV using KB mirrors with a step size of 200 nm and a dwell time of 2 ms. A total of 360 projections were obtained from 0-360°, thus a 1° interval, with a half degree off-set after 180° as to correct for any self-absorption events that might happen with XRF without duplicating collection angles. The acquisition time (including motor movement and initialization) for a single projection was 220 seconds and the total acquisition time of all projections was 22 hours. The Ti XRF raw data was fitted according to Solé et al., using PyMCA [8]. The raw data collected with PXCT consists of a far-field Fraunhofer diffraction pattern collected at each scanning point. Using an in-house developed iterative reconstruction algorithm the real part of the refractive index, $\delta(r)$, is then reconstructed for the object measured [9]. Due to the absence of a stable reference in this work with a known refractive index (air) in the FOV, the normalization was performed using the beam intensity without any rescaling of the real and imaginary part of the refractive index. This means that the real part of the refractive index, $\delta(r)$, measured here and therefore the local electron density, $\rho_e$, is in this case not quantitative. Future improvements such as upgrading to a 4th generation synchrotron leading to a higher and more
coherent photon flux, e.g. Max IV, ESRF EBS or the planned Petra IV, as well as detector improvements with higher scan-rates will allow the dwell-time per pixel to be reduced to sub-ms [10-12]. This would allow for larger FOV’s to be scanned without sacrificing precious allocated beam-time and thus incorporate a stable air reference for quantitative X-ray phase nano-tomography on polyolefin catalysts that require a large FOV (>140 µm in width if using these polyimide capillaries).

In Figure S4 a comparison is given of the first and 362nd PXCT projections, which are taken 22 hours of continuous scanning and therefore exposure to the X-ray beam apart. No significant beam-damage was observed in this work, whereas in our previous work we observed significant beam-damage most likely due to residual solvent molecules within the polyolefin phase [7]. It should be noted here that there is a 0.5° degree off-set between the two projections (0-180° and 180.5-360.5°).

![Figure S4 Comparison of the first and 362nd horizontally aligned PXCT projections taken respectively at the collection angles of 0° and 360.5° (constant increment of 1° with a 0.5° off-set after 180°). No significant beam-damage is observed during the 22 hours total scanning time.](image)

5. Tomography Reconstruction of the Ptychography X-ray Computed Tomography and X-ray Fluorescence Data-sets

All subsequent analytical and reconstruction procedures were performed on a workstation equipped with an Intel® Xeon® Gold 6242 CPU running at 2.80 GHz with 16 cores, 256 GB of DDR4 RAM memory running at 2933 MHz and a Nvidia® Quadra GV100 GPU. Typically around 20-50 GB of memory was occupied due to the size of the non-binned PXCT data-set and any subsequent 3-D operations. Tomographic reconstruction of the 3-D volume of the X-ray Ptychography and XRF 2-D projections was performed inside the TXM-Wizard software package [13]. After the collection of the first 180 projections a slight drift of the capillary was noticed due to mounting the capillary on the sample holder using clay and could be optimized further by switching to an epoxy glue instead. To obtain a high resolution 3-D reconstruction of the obtained data-sets, this drift together with any motor position inaccuracies has to be corrected for. Normally, in the ideal case of measuring an isolated spherical object with ample of empty space measured at all sides of the object, correcting for any movement is relatively simple. Strategies involve manually tracking the same feature(s) at each subsequent 2-D projection and using this as the center of rotation as well as the use of a registration algorithm to automatically find any displacement in both horizontal and vertical (or even tilting angle corrections) directions of the region of interest. A combination of both where at first a feature is tracked manually for a rough alignment followed by a registration algorithm for sub-pixel accuracy can be highly effective [14,15]. In this particular situation, the manual tracking isn’t feasible due to the difficulty of tracking the same feature(s) over the large FOV scanned consisting of many particles.
Instead the following combination was used for the alignment of the ROI to the rotation axis (horizontal alignment) of both the PXCT and XRF data-sets. No significant drift was observed in the vertical direction. Steps B to E are visualized in Figure S5 and a generalized flowchart is given in Figure S6:

A) The first step is to flip the 180.5 to 359.5° 2-D projections horizontally. This effectively makes the second half of the data-set go from 0.5° to 179.5° with a 1° increment. This step proved to be crucial for good results in the final alignment used in step D. The reason to collect the angles from 0-360° was to mitigate any possible self-absorption effects while collecting the Ti XRF data.

B) Inside the Avizo™ software package (due to its ease in visualization), the raw 2-D projections of both PXCT and XRF data-sets were binarized at a threshold at 10% of the grayscale values. This means that if the histogram of pixel intensities has a theoretical range from 0-100 then all values below 10 are set equal to 0 and all values above 10 are set equal to 1. This removes low-intensity noise from the first rough alignment performed in step C. Furthermore, in the case of PXCT the capillary wall is removed from each 2-D projection manually. It should be noted here that for the Ti XRF data-sets the capillary walls are not observed.

C) A first rough alignment to bring all ROI’s towards the center of image is performed as follows. For each horizontal line within the binarized image, the index of the center of the filled voxels (voxel value is 1) is found using an in-house developed Matlab® code. This is achieved by finding the index of the first and last value equal to 1 at each horizontal line and taking the average of these indexes as the center of the respective horizontal line. The average of index of all horizontal lines is then taken to be the horizontal center of that respective 2-D projection. This is then repeated in a loop for all 2-D projections. These values give the difference of the center of the horizontal dimension of a 2-D projection with regards to the center of the ROI inside this 2-D projection. To illustrate this: for a typical PXCT 2-D projection the horizontal center of the image is at a pixel value 1250 (total size is 2500 pixels in width) and if the center of the ROI is found to be at 1240 then a horizontal translation of 1250-1240 pixels = +10 pixels within Matlab®. The translation values necessary for each 2-D projections are then both applied to the thresholded and masked 2-D projections for the subsequent fine alignment in step D as well as saved in a text-file to perform later on the original and non-thresholded 2-D projections.

D) A registration algorithm between each thresholded and masked 2-D projection with the previous projection is then used for the fine alignment of the horizontal displacement. The Astra toolbox compatible with Matlab® was used for this purpose [14,15]. The translation values of the fine alignment were also saved in a text-file similar to step C.

E) The rough and fine alignment steps gave two text files of translation values. These were applied sequentially to the original 2-D projections after which the original 2-D projections were aligned successfully with respect to each other and still contain the full range of data.

F) During a typical filtered back projection (FBP) reconstruction with a Shepp-Logan filter of the central slice of each data-set, we noticed that the rotation center was still slightly off for the PXCT data-set. Using a horizontal off-set value of -20 pixels within the TXM-Wizard software package, the sharpest reconstructed central slice was obtained. This off-set value is similar to step C in the sense that it performs a horizontal translation but in this case the off-set value is equal for all 2-D projections.

G) Finally, all slices of the PXCT data-set were then reconstructed using the Shepp-Logan filter with a FBP reconstruction algorithm. Due to the low signal-to-noise ratio of the Ti XRF data-set, an iterative algebraic reconstruction algorithm (iART) was used in the TXM-Wizard software package.
Methodology used to align and correct for any horizontal drift of the sample. The 0° and 180° PXCT projections are shown for illustration. In step 1 the raw 2-D PXCT projections are binarized with a 10% threshold and the capillary wall is removed manually. In the second step, for each horizontal line the centre position is found based on the mean value of the first and last 1-valued pixels in that horizontal line (background has a value of 0 for each pixel in a binarized image). Then the mean horizontal centre position is calculated for the entire 2-D projection. In step 3 this mean value is used to perform a first rough translation on the masked images. These translation values are meanwhile also saved in a text-file. In step 4 a registration algorithm is applied as a fine refinement step, which aligns a 2-D projection to its previous 2-D projection and these translation values are again saved in a separate text-file. In step 5, the rough and fine alignment translations are applied to the original non-masked PXCT projections sequentially to finally obtain the PXCT projections aligned with respect to each other. In a final step not shown here, corrections for the off-set of the centre of rotation are optimized within the TXM-Wizard software to yield the best reconstructed 3-D volume.

Figure S5
Figure S6 (a) Acquisition and reconstruction of the 2-D X-ray ptychographic and fluorescence projections. (b) Alignment procedure of the 2-D projections followed by a 3-D filtered back projection (FBP) reconstruction and subsequent 3-D non-local means filtering to remove white-noise. (c) Manual marker drawing procedure followed by a marker-based watershed segmentation to isolate the particles not touching any borders. (d) Statistical analysis on the isolated particles as a whole to generate geometrical parameters (e.g. sphericity, equivalent spherical diameter, elongation) as well as intra-particle segmentation based on \(k\)-means clustering algorithm to separate the highly mixed polymer and catalyst phases to study the fragmentation behaviour.

The voxel size of the reconstructed PXCT data-set is 45.4x45.4x45.4 nm\(^3\) and that of the XRF data-set is 200x200x200 nm\(^3\). All subsequent volume rendering was performed in either the Avizo\textsuperscript{TM} software package or within Matlab\textsuperscript{©}. To remove noise from the reconstruction a 3-D non-local means (NLM) filter implemented within Avizo was used. One of the main advantages of this filter is that it assumes the noise to be white-noise and preserves the sharpness of strong edges. An example of the central slice in the XY plane before and after the 3-D NLM filter is shown below in Figure S7. An image registration algorithm within Avizo was used to align the XRF data-set to that of the PXCT. The reconstructed PXCT data-set is originally in a 32-bit float format, which allows for storing the raw quantitative electron density data if obtained. However, since in this work the electron density isn’t quantitative, most of the subsequent data-analysis was performed on a 16-bit unsigned converted data-set. This linearly scales all values into a format that can easily exported from Avizo as 2-D tiffs to be opened in Matlab\textsuperscript{©} when using in-house developed codes, without losing information on the relative position of each chemical phase.
Figure S7 (a) In blue contour, the central slices in the XY plane are given for the PXCT data-set before (left) and after (right) applying a non-local means (NLM) filter in 3-D to eliminate white-noise. (b) In red contour, the zoom-ins are given for a detailed comparison between the raw and NLM filtered data-sets.
6. Fourier Shell Correlation Estimation of the Achieved 3-D Spatial Resolution

To estimate the achieved 3-D spatial resolution of the PXCT and XRF data-sets, the Fourier Shell Correlation (FSC) technique was used [16,17]. The FSC estimated resolution was calculated by separating the original 2-D projections (after the alignment steps from section 5) in odd and even angles and performing a FBP reconstruction on each half data-set. These two reconstructed half data-sets should theoretically contain the same spatial information. Using the Fourier transform of both 3-D reconstructed volumes, their statistical correlation is calculated for each shell of constant spatial frequency with varying magnitude. A FSC curve plots this correlation going from low spatial frequency to high spatial frequency (1/voxel size) and the spatial resolution is then estimated as the cross-section of the correlation plot versus a chosen threshold value. Here the half-bit criterion is chosen as the value above which point the collected information can be reliably used to interpret the 3-D reconstructed volume.

In Figure S8 the FSC curves are given for the PXCT and XRF data-sets before any noise-reduction steps (raw reconstructions) using a Matlab® code from the Astra toolbox [14,15]. Both the 1-bit (full-bit) and ½-bit (half-bit) criterion estimated 3-D spatial resolution are given. When referred to the achieved 3-D spatial resolution in this work, the ½-bit criterion value is taken. For the PXCT data-set the achieved 3-D spatial resolution is 74 nm whereas for the Ti XRF data-set this is 217 nm.

![Fourier Shell Correlation (FSC) plots](image)

Figure S8 Fourier Shell Correlation (FSC) plots of (a) Ti XRF with 1/voxel size intersections of 0.74 for 1-bit and 0.92 for 1/2-bit giving estimated 3-D resolution values of respectively 270 and 217 nm and (b) PXCT with 1/voxel size intersections intersection of 0.47 for 1-bit and 0.61 for 1/2-bit giving estimated 3-D resolution values of respectively 97 and 74 nm.
7. Limited Information from the Ti X-ray Fluorescence Data-set

Despite the FSC estimated 3-D spatial resolution of 217 nm for the Ti XRF data-set assessment of the state of fragmentation within each catalyst particle didn’t work as done in our previous work where the system investigated was at a higher polymerization yield and therefore exhibited more pronounced and stronger catalyst support fragmentation [7]. In Figure S9 a comparison of the central slice of the Ti XRF and PXCT data-sets is given as well as a zoom-in for one randomly selected particle. It becomes clear that whereas PXCT shows clear regions of different intensity values with high resolution, which are the cracks of the catalyst framework most likely due to the polymerization, these features are not clearly visible within the Ti XRF data-set. This could simply be due to the fact that the 3-D spatial resolution of the Ti XRF data-set, albeit close to the 2-D pixel value, is about 3 times larger than the PXCT data-set. Additionally to the spatial resolution gap, the Si drift XRF detectors used in this work provided us with less counts in the FOV than with the previously used but now inoperable MAIA XRF detector [7]. Nonetheless, high quality Ti and even Cl and Mg XRF data-sets could be collected with improvements in the solid collection angles of the XRF detectors, smaller X-ray beam-and-step-size and switching to a He-filled (or vacuum) measuring chamber. This would change the attenuation length of Ti and Cl Kα photons at respectively ~4.5 ~2.6 keV from several centimeters and millimeters in air towards several tens of meters in He.

Figure S9 Visualizations of the reconstructed central slices in the XY plane of the Ti XRF data-set on the top-left with 200x200x200 nm voxel size and the PXCT data-set on the top-right with 45.4x45.4x45.4 nm voxel size. A zoom-in of the same 30x30 µm² area for both data-sets is given in the bottom row, which shows the clear difference in quality between the Ti XRF and PXCT data-sets.
8. Marker-based Watershed Segmentation

From the central slices in Figure S7, it becomes clear that many particles are present in the scanned FOV, which opens the route to a statistical analysis of the state of fragmentation of each individual particle. A common approach would be to first binarize the 3-D volume based on a certain threshold and then use a labelling procedure to assign each particle a unique identity. However, a labelling procedure performed directly on a PXCT binarized 3-D volume results in a severe underestimation of the number of composite particles imaged. The reason for this is the high connectivity between the composite particles as evidenced also by the agglomeration of the composite particles with SEM images in Figure S3. Morphological operations such as erosion or selective closing (dilation followed by erosion) could be used in an attempt to remove the connectivity between adjacent particles but this didn’t give satisfactory results for this PXCT data-set.

A different approach is to segment the 3-D reconstructed agglomeration into individual particles. A common approach is the so-called watershed segmentation algorithm [18]. This algorithm is based on finding the watershed ridge lines that separate catchment basins from each other. In this case, the catchment basin can be seen as the center of each particle and the watershed ridge lines would be defined at regions where the transition of low intensity voxels (background) to high intensity voxels (particle) is largest. The watershed segmentation process works best when providing some a priori knowledge about the position and number of particles expected through feeding the algorithm with markers. A common strategy to create these markers automatically is as follows:

A) Transform the grayscale volume into a binarized volume.
B) Calculate the distance map of the binarized volume, which gives the Euclidian distance between each voxel and the first non-zero voxel neighbors.
C) Use the inverted distance map to calculate the H-minima (ergo the position of each catchment basin), where H is a chosen value of the depth of this catchment basin from the watershed ridge lines where markers falling below this H-criterion are merged together to prevent over-segmentation.

However, despite the use of this H-criterion the non-supervised watershed segmentation algorithm is often plagued by either under- or oversegmentation. Therefore, in this case we chose for a more time-consuming approach by manually drawing the markers so as to have a strong control over the amount of particles are generated and to prevent both under- and over-segmentation that could otherwise occur with different H-values for the H-minima marker generation. To make a compromise between the time-consumption of drawing markers and its accuracy the following strategy was chosen (all steps performed in Avizo unless mentioned otherwise):

A) Resample the original data-set of 2500x2500x440 voxels to 625x625x110 voxels.
B) Draw the markers manually in the XY plane (110 instead of 440 slices due to the resampling step) on the resampled grayscale PXCT data-set whilst having cross-sectional views of the XZ and YZ planes open to confirm correct marker drawing. During this step it is highly important that different markers should not overlap in the 3-D volume or during the subsequent labelling procedure they will be assigned the same identity.
C) Resample the manually drawn markers back to the original size of 2500x2500x440 voxels.
D) Label the upscaled markers.
E) Binarize the original PXCT reconstructed volume using a manually found 10% threshold on the grayscale intensities. Using the near-full intensity histogram for the watershed segmentation would add too much background and noise signal to the labels and create unrealistically large particles.
F) However, the 10% thresholded binarized images underestimates the volume of each particle as we remove not only voxels belonging to the background but also part of each particle. To
counter-act this, the binarized images are dilated in a ball-expansion mode (isotropic expansion). In Figure S10, the mean intensity of each single voxel shell added on the PXCT NLM filtered grayscale images during dilation is shown to find the dilation factor threshold that should be used. Based on these values a turnover point was observed around a dilation factor of 5, which was therefore used as the threshold for dilation. The dilation of the binarized PXCT volume was performed using in-house developed code within Matlab\textsuperscript{©} on a 16 bit unsigned conversion of the original 32 bit float data-set.

G) The use of this dilation factor of 5 can potentially still add voxels to the binarized volume with a mean grayscale intensity value low enough that it should be assigned to a background voxel. In Figure S10, this background mean grayscale intensity value was obtained by looking at the plateau achieved at very large dilation factors. In this case, a plateau of a mean grayscale intensity value of 315 was found after 15 voxel dilation. All voxels from the PXCT grayscale data-set with a value equal or lower than 315 were then removed from the 5x dilated binarized volume to correct for background voxels added during dilation.

H) Create the distance map in 3-D from the corrected binarized PXCT volume in step G.

I) Invert this generated distance map.

J) Perform a marker-based watershed algorithm on the inverted distance map from step I using the upscaled labelled markers from step D. The chosen output of this algorithm is the catchment basins (meaning the separated particles).

K) The created catchment basins are automatically labelled but are still separated from each other through the calculated watershed ridge lines. The labels are therefore expanded isotropically to fill the full volume.

L) Finally, these labels are then masked by the corrected binarized volume from step G to give the separated composite polymer-catalyst particles with the entire background successfully removed.

These separated composite particles, each with its own unique label identity, can then be used for further analysis. However, from the 858 generated particles, 434 particles were partially cut-off by the lower and upper borders in the XY plane (as found by calculating the number of particles that have voxels interfacing any border). This means that these 434 particles, referred to as border particles, were not reconstructed completely due to the chosen FOV (as shown in main text Figure 1d schematically). After removal of these 434 incomplete particles, 424 completely imaged particles were obtained. These 424 separated particles were then saved as 16 bit unsigned 2-D tiff images to be opened in Matlab\textsuperscript{©}. Then in Matlab\textsuperscript{©} each of these 424 particles was visualized in 3-D using the maximum intensity projection volume rendering from the visualization toolbox. All particles were then inspected in terms of proper segmentation and several particles were found to instead consist of multiple particles. After manually correcting these faulty markers and redoing steps H-K, the final PXCT data-set was found to contain 434 separated and completely imaged particles.
9. Calculation of the Geometrical Parameters of Each Individual Ethylene Polymerized Catalyst Particle

After the marker-based watershed segmentation and subsequent removal of the incompletely reconstructed border particles, 434 separated and completely reconstructed ethylene polymerized catalyst particles remain. For each of these particles several geometrical parameters can be calculated using the label of each particle (meaning a binarized particle with an unique identity). A short explanation on the following geometrical parameters as calculated within either the Avizo software package or Matlab© is given:

1) The volume (V, µm³) of each particle. This is calculated by simply counting the number of non-zero voxels of each particle’s binarized image and multiplying this by the volume of a single voxel (~9.4E-05 µm³).

2) The surface area (SA, µm²) of each particle. This is calculated in Matlab© using the Crofton formula as described by Lehmann and Legland [19].

3) The particle’s equivalent spherical diameter (ESD in µm). This is calculated simply by assuming the particle to be a perfect sphere and using the following Eq. S2 based on the volume calculated in 1):

\[ ESD = \left( \frac{6 \cdot V}{\pi} \right)^{\frac{1}{3}} \] [Eq. S2]
4) The particle size distribution (PSD, µm) of each particle. Using the ESD values, the 10, 50 and 90 percentile distribution values referred to as respectively \(D_{10}\), \(D_{50}\) and \(D_{90}\) can be calculated as well as the span (unitless, see Eq. S1). These values can then be compared to other measurement techniques such as SLS or SEM as well as to the theoretically expected \(D_{50}\) based on the polymer yield as discussed in section S2.

The following particle metrics provide information about the shape of each particle and in the case of non-perfect spherical (elongated, spheroidal) also the preferred orientation of the elongation axis:

5) The sphericity (\(\Psi\), unitless) of each particle. The sphericity is defined as the ratio of the surface area of a perfect sphere that encloses the same volume as the surface area of the particle, see Eq. S3. For a perfect sphere the ratio is therefore 1 and any object deviating from a perfect sphere will have a value lower than 1

\[
\Psi = \frac{n^2 \times (6 \times V_p)^{\frac{2}{3}}}{S_A p} \quad \text{[Eq. S3]}
\]

6) The elongation (unitless) of each particle. The elongation provides additional information on the preferred orientation of a particle’s shape along a certain direction. The elongation value is calculated based on the ratio of the medium and largest eigenvalues of the covariance matrix of each particle as explained by Meirer et al., [20]. A perfect sphere will have an elongation value of 1 as all eigenvalues are equal, whereas a highly elongated particle shape will have a value close to 0. In the case of values below 1, the orientation of the largest or first eigenvalue can be visualized in 3-D to show if there is any preferred orientation of the elongation axis of all the particles within the agglomeration (see main text Figure 3a). To do so, the classic Euler angles, i.e. yaw and pitch, were used to show the particle orientation with respect to the same fixed coordinate system used for all ethylene polymerization catalyst particles [21].

7) The flatness (unitless) of each particle. The flatness is calculated as the ratio of the smallest to the medium eigenvalues of the covariance matrix of each particle.

10. K-Means clustering algorithm

The grayscale values reported here are the real part of the refractive index, \(\delta(r)\), which is linearly related to the local electron density, \(\rho_e (e/Å^3)\), as shown in Eq. S4, where \(r_0\) is the Thompson scattering length (alternatively known as the classical electron radius, \(r_e\)) and \(\lambda\) is the wavelength of the X-ray probe used in angstroms. In quantitative X-ray phase nanotomography, the local electron density measured can be directly compared to the calculated total electron density of a mixture of compounds assuming the atomic composition within a voxel is known. This formula is shown in Eq. S5, where \(N_A\) is Avogadro’s constant, \(\rho_m\) is the total mass density, \(W_j\), \(Z_j\) and \(M_j\) are respectively the weight percentage, number of electrons and molar mass of the j-th compound [22].

\[
\rho_e (r) = \frac{2n\delta(r)}{r_0 \lambda^2} \quad \text{[Eq. S4]}
\]

\[
\rho_e = N_A \rho_m \sum_j W_j \frac{Z_j}{M_j} \quad \text{[Eq. S5]}
\]
Since in this situation the obtained real part of the refractive index and therefore local electron density are not properly scaled versus a stable reference, a comparison with a calculated total electron density from Eq. S5 isn’t feasible. Furthermore, the histogram of the grayscale intensity values in Figure S11 shows a broad distribution where it is difficult to discriminate between a HDPE and Ziegler-catalyst phase. This is most likely the result of the high degree of mixing of HDPE and Ziegler catalyst phases beyond the achieved 3-D spatial resolution of 74 nm. For example, the Ziegler-catalyst shows exclusively mesoporosity with pore sizes between 20-50 nm as discussed in section S1. This means that even at the earliest stages of ethylene polymerization where HDPE is forming within the pore network but the stress exerted on the framework hasn’t reach a threshold yet to cause fragmentation, considerable sub-spatial resolution mixing of two chemical phases is expected. The mass density of the HDPE and Ziegler-catalyst phases are assumed to be on the order of ~0.95 g/cm\(^3\) for HDPE and ~2.32 g/cm\(^3\) for anhydrous MgCl\(_2\) (the framework of a Ziegler-catalyst). Therefore the high degree of mixing of both phases below the achieved spatial resolution and with a high difference in the mass density and therefore the electron density of each material is expected to be the reason for this broadening of the grayscale intensity values.

Applying a manual threshold on the grayscale intensities to what could be considered a HDPE phase and a Ziegler-catalyst phase would be subjective and open for interpretation in this difficult situation. However, the K-means clustering method provides an efficient way to partition each data-point, \(n\), in this case a grayscale intensity value, to the nearest mean position of a cluster \(K\). Here the number of K-clusters is chosen manually and the mean of each \(K\), called the centroid, is initialized through a so called K\(^++\)-algorithm within Matlab\textsuperscript©, which uses an heuristic method to find the centroid seeds for the K-means clustering [23].

Four K-clusters were chosen, where each K-cluster is expected to represent the following chemical phases in ascending order of mean electron density: \(K_1\) should represent a chemical phase dominant in HDPE since HDPE has the lowest mass density and therefore a lower electron density according to Eq. S5 than the Ziegler catalyst. \(K_2\) and \(K_3\) both represent highly mixed phases of HDPE and the Ziegler catalyst where in \(K_2\) and \(K_3\) the molar fraction in a voxel are highest for respectively HDPE in \(K_2\) and the Ziegler catalyst in \(K_3\). Finally, \(K_4\) has the highest mean electron density of all \(k\)-means clusters and should therefore represent a chemical phase dominant in the Ziegler catalyst. The result of the partitioning of the PXCT grayscale intensity histogram in these four different K-means clusters is shown in Figure S11. Furthermore, the geometrical parameters similar as to those given in Table 1 for the full particles are given here for each K-means cluster within each particle in Table S1.

The motivation for 4 \(k\)-means clusters instead of 3 \(k\)-means clusters where one could rationalize only a close-to-pure HDPE cluster, highly mixed HDPE and catalyst cluster and close-to-pure catalyst cluster is based on the calculated ESD of the clusters. As shown in Table S1, the ESD for the close-to-pure catalyst \(K_4\) cluster is 3.10 \(\mu\)m, which is 14.8% smaller than that of the pure pristine catalyst \(D_{50}\) of 3.64 \(\mu\)m. With 3 instead of 4 \(k\)-means clusters, the calculated ESD of the close-to-pure catalyst cluster (\(K_3\) in that case, since there are only 3 clusters) would be 3.66 \(\mu\)m and is practically equal to that of the pristine catalyst. Whereas, this might seem logical at first, this would mean that the \(K_1\) and \(K_2\) clusters should both represent a pure HDPE phase since all catalyst is now contained in the \(K_3\) cluster. However, the histogram of the combined \(K_{1,2}\) in the case of 4 clusters is already too broad and non-gaussian in peak-shape to describe a single chemical phase. Therefore, with 3 \(k\)-means clusters, a good portion of the highly mixed HDPE-catalyst phase is wrongfully assigned to the close-to-pure catalyst cluster \(K_3\) and therefore overestimates the spatially-resolved catalyst.
Figure S11. Histogram of the 16-bit unsigned converted PXCT grayscale intensity values after applying the 3-D non-local means filter. The color-coding from light blue to light green, orange and dark red correspond to the partitioning of the grayscale intensity values to four clusters (K$_1$ to K$_4$) using a k-means clustering algorithm. It should be noted here that the PXCT grayscale intensity values of the x-axis are of a 16-bit unsigned converted data-set (original is 32-bit float). This has no consequences for the data-analysis applied here since the raw data obtained doesn’t contain the quantitative mean electron density in each voxel.

Table S1. Overview of the mean and standard deviation values of the volume (V), surface area (SA) and equivalent spherical diameter (ESD), the 10,50,90 percentile fraction of particle size (D$_x$) and their span, sphericity (Ψ) for the four k-means clusters of all 434 ethylene polymerized catalyst particles.

| Particle Metrics | K$_1$        | K$_2$        | K$_3$        | K$_4$        |
|------------------|--------------|--------------|--------------|--------------|
| V (μm$^3$)       | 33.6 ± 18.7  | 24.6 ± 17.7  | 31.6 ± 27.3  | 19.7 ± 20.4  |
| SA (μm$^2$)      | 265.3 ± 145.6| 304.5 ± 210.8| 291.9 ± 239.4| 129.2 ± 116.7|
| ESD (μm)         | 3.89 ± 0.65  | 3.46 ± 0.71  | 3.71 ± 0.89  | 3.10 ± 0.88  |
| D$_{10}$ (μm)    | 3.20         | 2.69         | 2.67         | 2.09         |
| D$_{50}$ (μm)    | 3.85         | 3.40         | 3.66         | 3.02         |
| D$_{90}$ (μm)    | 4.62         | 4.25         | 4.63         | 4.15         |
| Span             | 0.37         | 0.46         | 0.53         | 0.68         |
| Ψ                | 0.20         | 0.026        | 0.04         | 0.08         |

11. Calculation and comparison of different candidate fragmentation parameters

Besides the main fragmentation parameter, V$_r$, used to study the degree of catalyst fragmentation, additional fragmentation parameters can be designed and tried. These additional fragmentation parameters include standard image textural analysis techniques such as calculating the entropy, which is a measurement of the distribution of the greyscale intensity values within a particle, but also the calculation of the total number of spatially resolved catalyst fragments in the K$_4$ cluster, referred to as N$_{NCC}$ and the sum distance of these catalyst fragments to the particles center, referred to as D$_{NCC-center}$. Fundamentally speaking both a pure catalyst particle and a pure HDPE particle will have similar low entropy and standard deviation values due to the presence of a narrow greyscale intensity distribution. Therefore, such textural analysis techniques can’t distinguish between extreme cases of very low and very high degrees of catalyst fragmentation due to the complete lack of chemical information input. Alternatively, the N$_{NCC}$ and D$_{NCC-center}$ fragmentation parameters are fundamentally more
straightforward than $V_r$ as they directly and purely consider the catalyst fragments to study the degree of catalyst fragmentation. However, since both of these fragmentation parameters fully rely on being able to spatially resolve all catalyst fragments in the $K_4$ cluster to quantify the fragmentation degree it can severely underestimate the catalyst fragmentation degree in this study. The reason for this is that the smallest or also called primary particle size of the MgCl$_2$ support matrix is reported on the order of several to several tens of nm whereas the achieved spatial resolution in this work is 74 nm. Therefore, both catalyst fragments smaller than 74 nm and catalyst fragments in close proximity of each other can be either assigned to a lower $k$-means cluster and thus removed from the fragmentation parameter or become assigned to a single larger fragment.

The three fragmentation parameters used to study the degree or state of fragmentation of each particle are calculated in Matlab$^\text{©}$ using in-house written code:

A) The main fragmentation parameter, $V_r$, used in this work is based on the ratio of the total volume of the $K_{1,2,3}$ clusters, which constitute the formed HDPE and catalyst fragments that couldn’t be spatially resolved from the mixing with HDPE, to the mean volume of the catalyst fragments in the $K_4$ cluster. This $V_r$ value is calculated by summing the $K_{1,2,3}$ volumes up for each particle and dividing this by the mean volume of all non-connected components (NCCs) found in $K_4$. These NCCs are found by performing a labelling procedure on $K_4$ similar as to that performed after the watershed segmentation described in section 8.

B) By counting the total number of NCCs in each particle and sort them accordingly in terms of increasing fragmentation degree the $N_{\text{NCC}}$ fragmentation parameter is constructed. This $N_{\text{NCC}}$ is calculated as described for $V_r$ by counting the total number of NCCs found in $K_4$ for each particle. $N_{\text{NCC}}$ suffers from underestimation of the fragmentation parameter since only spatially resolved catalyst fragments in the $K_4$ cluster are considered.

C) Finally, by also taking the distance of the NCCs from the center into account, additional spatial information is added to $N_{\text{NCC}}$ in the form of the $D_{\text{NCC-center}}$ fragmentation parameter. However, $D_{\text{NCC-center}}$ suffers from the same shortcoming as $N_{\text{NCC}}$ in that it fragments that are spatially unresolved from the HDPE phase are not taken into account. To calculate the sum of the distance of the NCCs in $K_4$ to the respective particle’s center for each particle ($D_{\text{NCC-center}}$) the Euclidean distance is measured between the centroid of each NCC and the centroid of a particle.

Using the values obtained from the fragmentation parameter calculations of each particle, a sorting procedure can be made. In this sorting procedure, each particle gets assigned an ID value based on the value obtained from the respective fragmentation parameter in ascending order. For example, imagine a scenario with only two particles imaged. Particle A has a $N_{\text{NCC}}$ value of 1 and a $V_r$ value of 10 and particle B has a $N_{\text{NCC}}$ value of 10 and $V_r$ value of 1. In this case Particle A would be assigned an ID value of 1 for $N_{\text{NCC}}$ since it has a lower $N_{\text{NCC}}$ value than particle B. However, particle A would be assigned an ID value of 2 for $V_r$ since it has a larger $V_r$ than particle B. Furthermore, a sorting parameter dispersion is calculated for each particle, which is simply the standard deviation value of the ID value this particle gets assigned according to each of the four fragmentation parameters. A small sorting dispersion value thus means that all three fragmentation parameters are in good agreement with each other regarding the degree of catalyst fragmentation of that specific particle. A large sorting dispersion value means that there is a weak agreement between these three fragmentation parameters regarding the degree
of catalyst fragmentation of that specific composite particle. A weak agreement is typically expected for certain composite particles where the achieved 3-D spatial resolution limits the assessment of one or more of the three fragmentation parameters. In Table S2 the sorting ID values of all three fragmentation parameters are shown in an ascending order with respect to the sorting dispersion.

Table S2. Overview of the fragmentation parameter sorting dispersion and the sorting value of all 434 composite particles as assessed by \( V_r \), \( N_{NCC} \) and \( D_{NCC-center} \). The sorting dispersion is calculated as the standard deviation of the sorting value each particle gets assigned according to these three fragmentation parameters, \( V_r \), \( N_{NCC} \) and \( D_{NCC-center} \). The contents of the tables are given in an ascending order of the sorting dispersion. Particles with a low sorting dispersion have a strong agreement in the sorting between all three fragmentation parameters regardless of whether it is sorted in an early or late stage of fragmentation whereas particles with a high sorting dispersion show a weaker agreement between the fragmentation parameters used.

| Sorting Dispersion | Fragmentation Parameter | Sorting Dispersion | Fragmentation Parameter |
|--------------------|-------------------------|--------------------|-------------------------|
| 0                  | \( V_r \) 434 \( N_{NCC} \) 434 | 8.7                | \( V_r \) 406 \( N_{NCC} \) 422 |
| 0.6                | 12 13 13 | 9                  | 261 269 251 |
| 1                  | 1 3 2 | 9.2                | 140 152 158 |
| 1                  | 410 411 412 | 9.6                | 43 40 25 |
| 1.2                | 3 1 1 | 9.6                | 81 99 96 |
| 1.2                | 427 427 429 | 9.8                | 428 409 414 |
| 1.5                | 63 61 60 | 10                 | 404 415 424 |
| 1.5                | 386 384 387 | 10.5               | 155 176 165 |
| 1.7                | 4 7 4 | 10.8               | 390 373 393 |
| 2.5                | 5 2 7 | 11                 | 16 36 18 |
| 3.1                | 2 8 6 | 11.1               | 337 328 350 |
| 3.5                | 15 18 22 | 11.2               | 307 286 290 |
| 3.8                | 426 433 432 | 11.2               | 412 429 433 |
| 4.4                | 409 417 410 | 11.5               | 388 377 400 |
| 5.2                | 69 69 78 | 11.7               | 20 28 5 |
| 5.6                | 395 388 399 | 12                 | 327 351 339 |
| 5.7                | 21 24 32 | 12.1               | 397 407 421 |
| 6.1                | 27 26 16 | 12.1               | 13 22 37 |
| 6.4                | 401 412 401 | 12.2               | 25 5 3 |
| 6.5                | 17 4 10 | 12.2               | 115 113 135 |
| 6.6                | 400 387 395 | 12.7               | 398 414 423 |
| 6.7                | 11 20 24 | 12.7               | 403 422 427 |
| 7                  | 331 325 317 | 13                 | 306 305 283 |
| 7.4                | 373 362 376 | 13                 | 59 33 47 |
| 7.4                | 417 428 431 | 13.1               | 389 364 370 |
| 7.5                | 317 324 332 | 13.5               | 29 44 56 |
| 7.6                | 411 421 426 | 13.6               | 216 217 193 |
| 7.8                | 8 12 23 | 13.7               | 7 17 34 |
| 7.8                | 35 50 39 | 13.7               | 36 58 61 |
| 7.8                | 91 80 95 | 13.8               | 10 15 36 |
| 7.8                | 339 338 352 | 14                 | 32 39 59 |
| 7.8                | 433 432 419 | 14.2               | 28 54 51 |
| 8.2                | 358 374 369 | 14.4               | 78 78 103 |
| 8.4                | 24 23 9 | 14.5               | 9 11 35 |
| 8.5                | 345 361 348 | 14.5               | 137 135 161 |
| 8.5                | 82 91 74 | 15.3               | 425 395 415 |
| 8.7                | 405 391 389 | 15.5               | 177 160 146 |
| Sorting Dispersion | Fragmentation Parameter |  |
|--------------------|------------------------|---|
|                    | $V_f$ | $N_{NCC}$ | $D_{NCC-center}$ |  |
| 15.5               | 408   | 425       | 394              |  |
| 15.7               | 37    | 41        | 12               |  |
| 16                 | 123   | 108       | 91               |  |
| 16.3               | 343   | 332       | 364              |  |
| 16.4               | 52    | 30        | 20               |  |
| 16.4               | 424   | 393       | 418              |  |
| 16.5               | 402   | 431       | 430              |  |
| 16.7               | 225   | 196       | 225              |  |
| 16.8               | 383   | 355       | 353              |  |
| 17                 | 126   | 107       | 141              |  |
| 17                 | 129   | 159       | 130              |  |
| 17.2               | 156   | 181       | 189              |  |
| 17.2               | 336   | 363       | 331              |  |
| 17.2               | 384   | 389       | 416              |  |
| 17.2               | 34    | 56        | 68               |  |
| 17.5               | 44    | 9         | 26               |  |
| 18                 | 298   | 265       | 294              |  |
| 18.3               | 319   | 292       | 284              |  |
| 18.4               | 360   | 349       | 385              |  |
| 18.5               | 72    | 35        | 52               |  |
| 18.6               | 98    | 94        | 128              |  |
| 18.6               | 382   | 367       | 404              |  |
| 18.6               | 416   | 401       | 379              |  |
| 18.9               | 349   | 386       | 374              |  |
| 19                 | 105   | 87        | 125              |  |
| 19.1               | 128   | 165       | 155              |  |
| 19.7               | 351   | 381       | 388              |  |
| 19.9               | 285   | 316       | 322              |  |
| 19.9               | 292   | 291       | 326              |  |
| 20                 | 41    | 77        | 44               |  |
| 20                 | 323   | 304       | 344              |  |
| 20.1               | 421   | 410       | 382              |  |
| 20.6               | 86    | 119       | 124              |  |
| 20.8               | 46    | 53        | 85               |  |
| 21                 | 423   | 400       | 381              |  |
| 21.5               | 189   | 193       | 228              |  |
| 21.7               | 255   | 254       | 217              |  |
| 21.7               | 249   | 222       | 265              |  |
| 22.1               | 110   | 92        | 136              |  |
| 22.2               | 329   | 368       | 330              |  |
| 22.3               | 53    | 81        | 97               |  |
| 22.4               | 407   | 371       | 366              |  |
| 22.6               | 6     | 19        | 50               |  |
| 23                 | 418   | 372       | 397              |  |
| 23.1               | 47    | 74        | 28               |  |
| 23.1               | 114   | 73        | 75               |  |
| 23.2               | 45    | 32        | 77               |  |
| 23.3               | 374   | 380       | 417              |  |
| 23.4               | 169   | 161       | 205              |  |
| 23.5               | 33    | 38        | 76               |  |
| 24                 | 242   | 220       | 194              |  |
| 24.2               | 57    | 64        | 19               |  |
| Sorting Dispersion | Fragmentation Parameter | Sorting Dispersion | Fragmentation Parameter |
|--------------------|-------------------------|--------------------|-------------------------|
|                    | $V_f$ | $N_{NCC}$ | $D_{NCC-center}$ |                    | $V_f$ | $N_{NCC}$ | $D_{NCC-center}$ |
| 31.4               | 324   | 266     | 274             | 39.6               | 164   | 237     | 174             |
| 31.6               | 152   | 117     | 180             | 39.7               | 315   | 390     | 375             |
| 31.6               | 368   | 378     | 319             | 39.7               | 218   | 192     | 270             |
| 31.6               | 118   | 57      | 73              | 39.9               | 58    | 47      | 121             |
| 31.8               | 387   | 326     | 372             | 40                  | 303   | 344     | 383             |
| 32.1               | 338   | 317     | 380             | 40.2               | 223   | 145     | 167             |
| 32.2               | 301   | 339     | 365             | 40.3               | 431   | 416     | 355             |
| 32.4               | 222   | 177     | 159             | 40.3               | 356   | 293     | 368             |
| 32.5               | 139   | 204     | 170             | 40.5               | 22    | 46      | 101             |
| 32.5               | 214   | 279     | 245             | 40.6               | 170   | 231     | 154             |
| 32.5               | 275   | 336     | 325             | 40.6               | 102   | 115     | 178             |
| 33.5               | 226   | 191     | 258             | 40.7               | 113   | 183     | 112             |
| 33.5               | 252   | 185     | 221             | 40.7               | 124   | 134     | 199             |
| 33.6               | 40    | 84      | 106             | 41                  | 228   | 230     | 300             |
| 33.6               | 364   | 370     | 309             | 41.1               | 420   | 340     | 396             |
| 34.8               | 294   | 346     | 360             | 41.4               | 208   | 127     | 153             |
| 35.1               | 333   | 379     | 402             | 41.6               | 163   | 199     | 246             |
| 35.2               | 344   | 405     | 405             | 41.7               | 116   | 164     | 81              |
| 35.3               | 235   | 298     | 239             | 41.9               | 330   | 397     | 407             |
| 35.4               | 244   | 261     | 312             | 41.9               | 153   | 209     | 127             |
| 35.6               | 267   | 283     | 215             | 42.5               | 363   | 323     | 278             |
| 36.1               | 84    | 97      | 152             | 42.7               | 131   | 186     | 102             |
| 36.1               | 186   | 243     | 253             | 43                  | 120   | 206     | 162             |
| 36.2               | 103   | 122     | 173             | 43                  | 266   | 235     | 181             |
| 36.4               | 71    | 67      | 132             | 43                  | 353   | 267     | 308             |
| 36.5               | 64    | 114     | 43              | 43.5               | 31    | 63      | 117             |
| 36.5               | 217   | 148     | 203             | 43.5               | 195   | 179     | 113             |
| 36.8               | 286   | 213     | 242             | 43.5               | 283   | 241     | 328             |
| 36.8               | 289   | 333     | 362             | 43.7               | 211   | 262     | 298             |
| 37.2               | 393   | 413     | 341             | 44                  | 143   | 70      | 64              |
| 37.2               | 231   | 244     | 301             | 44                  | 176   | 203     | 262             |
| 37.2               | 93    | 29      | 94              | 44.2               | 215   | 197     | 281             |
| 37.4               | 109   | 121     | 179             | 44.6               | 125   | 138     | 208             |
| 37.6               | 207   | 248     | 282             | 44.9               | 135   | 123     | 206             |
| 37.7               | 288   | 308     | 361             | 44.9               | 119   | 126     | 45              |
| 37.8               | 415   | 341     | 391             | 46.2               | 70    | 149     | 151             |
| 37.8               | 342   | 345     | 409             | 46.3               | 106   | 90      | 177             |
| 38                 | 265   | 238     | 313             | 46.6               | 347   | 273     | 359             |
| 38                 | 302   | 343     | 378             | 46.7               | 335   | 423     | 406             |
| 38.2               | 38    | 55      | 111             | 46.8               | 133   | 51      | 53              |
| 38.2               | 399   | 430     | 354             | 48                  | 108   | 158     | 62              |
| 38.4               | 279   | 276     | 211             | 48.1               | 320   | 224     | 276             |
| 38.5               | 273   | 322     | 349             | 48.2               | 100   | 79      | 171             |
| 38.6               | 49    | 105     | 123             | 48.3               | 166   | 103     | 71              |
| 38.8               | 296   | 353     | 279             | 48.5               | 184   | 281     | 230             |
| 39                 | 284   | 359     | 340             | 48.6               | 74    | 93      | 166             |
| 39.1               | 290   | 360     | 295             | 49.1               | 316   | 247     | 342             |
| 39.1               | 136   | 86      | 163             | 49.1               | 19    | 85      | 115             |
| 39.3               | 159   | 112     | 190             | 49.1               | 354   | 258     | 324             |
| 39.5               | 334   | 406     | 398             | 49.2               | 51    | 139     | 133             |
| 39.5               | 341   | 264     | 287             | 49.8               | 112   | 14      | 48              |
| 39.6               | 157   | 147     | 84              | 49.9               | 300   | 299     | 213             |
| Sorting Dispersion | Dispersion Sorting | Fragmentation Parameter | Sorting Dispersion | Dispersion Sorting | Fragmentation Parameter |
|---------------------|--------------------|-------------------------|---------------------|--------------------|-------------------------|
| 50.4                |                    | 230 313 321             | 59.3                |                    | 313 420 411            |
| 50.9                |                    | 232 162 261             | 59.4                |                    | 77 174 66              |
| 51.3                |                    | 238 252 333             | 59.8                |                    | 168 163 269            |
| 51.6                |                    | 212 277 314             | 60.2                |                    | 221 251 337            |
| 51.6                |                    | 305 404 329             | 60.7                |                    | 340 221 260            |
| 51.7                |                    | 245 201 304             | 60.7                |                    | 357 236 305            |
| 52                  |                    | 104 106 195             | 60.7                |                    | 172 88 54              |
| 52.2                |                    | 96 155 200              | 61.5                |                    | 227 268 147            |
| 52.2                |                    | 422 318 363             | 61.6                |                    | 191 314 248            |
| 52.2                |                    | 326 358 256             | 61.6                |                    | 56 150 172             |
| 52.2                |                    | 39 76 142               | 61.7                |                    | 206 116 234            |
| 52.4                |                    | 378 295 392             | 61.7                |                    | 202 300 316            |
| 52.6                |                    | 392 287 345             | 62                  |                    | 219 242 336            |
| 52.6                |                    | 144 43 119              | 62.2                |                    | 121 96 214             |
| 52.6                |                    | 193 187 99              | 62.2                |                    | 209 184 302            |
| 52.9                |                    | 142 48 137              | 62.8                |                    | 419 294 367            |
| 52.9                |                    | 48 68 148               | 63                  |                    | 352 226 286            |
| 53.1                |                    | 299 347 241             | 63.2                |                    | 258 140 160            |
| 53.3                |                    | 210 166 272             | 63.2                |                    | 269 146 182            |
| 53.3                |                    | 314 382 277             | 63.6                |                    | 75 133 202             |
| 53.3                |                    | 196 284 292             | 64.2                |                    | 160 275 267            |
| 53.3                |                    | 132 175 238             | 64.5                |                    | 350 306 223            |
| 53.8                |                    | 414 310 386             | 65                  |                    | 76 98 198              |
| 53.8                |                    | 295 188 231             | 65.7                |                    | 68 111 197             |
| 54.1                |                    | 240 337 247             | 65.8                |                    | 150 171 273            |
| 54.2                |                    | 257 154 176             | 66                  |                    | 413 285 377            |
| 54.4                |                    | 145 216 252             | 66.6                |                    | 88 128 218             |
| 54.8                |                    | 179 223 288             | 66.8                |                    | 79 110 207             |
| 55.2                |                    | 362 357 264             | 68.4                |                    | 429 296 335            |
| 55.3                |                    | 187 225 296             | 68.4                |                    | 204 169 72             |
| 56.1                |                    | 203 190 100             | 68.6                |                    | 205 194 318            |
| 56.3                |                    | 138 141 237             | 68.9                |                    | 122 157 255            |
| 56.5                |                    | 246 320 357             | 68.9                |                    | 247 212 114            |
| 56.6                |                    | 62 151 46               | 69.1                |                    | 282 394 408            |
| 56.7                |                    | 325 426 420             | 69.2                |                    | 158 131 27             |
| 56.7                |                    | 149 173 257             | 69.4                |                    | 263 375 390            |
| 56.9                |                    | 304 205 303             | 70                  |                    | 167 233 307            |
| 56.9                |                    | 371 348 263             | 70.2                |                    | 254 365 384            |
| 56.9                |                    | 369 260 343             | 70.7                |                    | 277 302 169            |
| 57                  |                    | 308 402 299             | 71.3                |                    | 42 101 184             |
| 57.3                |                    | 65 172 83               | 71.6                |                    | 253 392 293            |
| 57.4                |                    | 293 278 187             | 71.6                |                    | 268 334 191            |
| 57.6                |                    | 134 198 249             | 72                  |                    | 372 240 356            |
| 57.6                |                    | 377 290 268             | 72.2                |                    | 148 202 291            |
| 57.8                |                    | 264 350 240             | 72.5                |                    | 99 214 233             |
| 58.4                |                    | 250 143 156             | 72.6                |                    | 259 120 226            |
| 58.4                |                    | 111 6 14                | 72.7                |                    | 130 170 29             |
| 58.5                |                    | 346 356 250             | 73.3                |                    | 328 354 216            |
| 58.8                |                    | 117 153 38              | 74.3                |                    | 391 398 266            |
| 59.1                |                    | 198 271 315             | 74.8                |                    | 271 385 244            |
| 59.2                |                    | 192 218 105             | 75.3                |                    | 376 342 232            |
| 59.3                |                    | 178 109 227             | 75.7                |                    | 367 239 373            |
| Sorting Dispersion | Fragmentation Parameter | \( V_t \) | \( N_{\text{NCC}} \) | \( D_{\text{NCC-center}} \) |
|--------------------|-------------------------|-----------|-------------|------------------|
| 76.3               | 213                     | 65        | 107         |
| 76.6               | 248                     | 257       | 120         |
| 77.3               | 181                     | 168       | 41          |
| 77.7               | 234                     | 253       | 110         |
| 78                 | 291                     | 137       | 192         |
| 78.9               | 381                     | 289       | 224         |
| 79.4               | 199                     | 229       | 79          |
| 79.5               | 251                     | 125       | 104         |
| 79.5               | 173                     | 331       | 236         |
| 80.4               | 297                     | 280       | 150         |
| 80.4               | 237                     | 215       | 88          |
| 83.4               | 188                     | 309       | 149         |
| 83.4               | 318                     | 321       | 175         |
| 84.1               | 89                      | 200       | 254         |
| 84.9               | 201                     | 167       | 40          |
| 84.9               | 146                     | 263       | 311         |
| 85.5               | 180                     | 335       | 320         |
| 85.6               | 220                     | 288       | 118         |
| 85.6               | 147                     | 274       | 310         |
| 86.8               | 385                     | 311       | 212         |
| 87.2               | 182                     | 180       | 30          |
| 88                 | 430                     | 255       | 327         |
| 88                 | 312                     | 136       | 222         |
| 88.5               | 66                      | 156       | 243         |
| 88.7               | 274                     | 312       | 143         |
| 89.5               | 185                     | 272       | 93          |
| 89.7               | 197                     | 31        | 55          |
| 90                 | 165                     | 303       | 334         |
| 92.5               | 233                     | 52        | 109         |
| 93.6               | 171                     | 256       | 69          |
| 93.9               | 432                     | 245       | 323         |
| 94.5               | 375                     | 195       | 235         |
| 95.1               | 370                     | 246       | 183         |
| 98.1               | 262                     | 66        | 157         |
| 98.6               | 239                     | 228       | 63          |
| 100.7              | 281                     | 227       | 86          |
| 101.4              | 278                     | 250       | 90          |
| 102.8              | 229                     | 178       | 31          |
| 103                | 95                      | 259       | 285         |
| 103.5              | 200                     | 27        | 15          |
| 103.8              | 272                     | 182       | 65          |
| 104.8              | 322                     | 319       | 139         |
| 105.9              | 332                     | 366       | 168         |
| 113.2              | 309                     | 352       | 138         |
| 124.2              | 276                     | 37        | 98          |
| 125.2              | 127                     | 376       | 275         |
| 137.4              | 355                     | 282       | 89          |
| 144.2              | 365                     | 102       | 131         |
12. Radial and Disk Analysis to Study the Fragmentation Behavior

In Figure 5 both the radial distribution of the all k-means clusters as well as a disk analysis on the mean grayscale intensity values is given along the XY plane. For both calculations the PXCT grayscale, PXCT labelled and k-means clustered data-sets were imported as 2-D Tiffs and analyzed with in-house developed Matlab® codes.

The radial distribution of the k-means clusters was calculated by starting at the surface of a particle and measuring the volume fraction of each k-means cluster. Then an erosion procedure of 1 voxel is initiated and the volume fraction of each k-means cluster is recalculated at this newly exposed particle surface. This is repeated until finally the center voxel(s) is reached. A detailed description of the radial distribution calculation is given by Meirer et al. [20]

For the disk analysis, each particle is analyzed along the XY plane starting from one end of the particle’s volume to the opposite. Along this XY plane, the particle is build up from certain number of slices where the distance or step size between each slice is defined by the size of a voxel, so 45.4 nm. Then at each slice the mean grayscale intensity is calculated over all voxels present within that slice and tabulated. The final plot gives the grayscale intensity at a slice number going from one end of the particle to the next. Therefore the center of the plot corresponds to the center of the particle’s respective volume.

13. Estimating the Distribution of Particles in Fragmentation State

The histogram of the $V_f$ fragmentation parameter including the k-means clustering analysis to partition the particles as either weak, moderate or strong degree of catalyst fragmentation is given in Figure S12. The methodology of this k-means clustering algorithm is identical to that as described in section 10 and here applied on the $V_f$ fragmentation parameter values. However, caution should be taken in interpreting these values as this k-means clustering algorithm will define hard boundaries on whether a particle is classified as weak, moderate or strong with regards to the fragmentation degree and in reality one would rather expect a smooth transition. Keeping this in mind, the k-means clustering algorithm with therefore 3 clusters, estimates that respectively 274, 123 and 37 polymerized catalyst particles show a weak, moderate and strong degree of catalyst fragmentation.
Figure S12. Histogram of the $V_r$ fragmentation parameter including the partitioning of the polymerized catalyst particles into either a weak (green), moderate (purple) or strong (red) degree of catalyst fragmentation through a $k$-means clustering algorithm ($3 \ k$-clusters). The hard boundaries give here between these three fragmentation classes are merely an estimation as one would expect a gradual transition from a weak to a strong degree of catalyst fragmentation. 274 particles are assigned to the weak, 123 to the moderate and 37 to the strong classification.

14. Supporting Movies

Movie S1:
At first the electron density of the entire reconstructed PXCT volume is shown before performing the marker-based watershed segmentation both by rotating the entire volume as well as by going through the volume with a clipping plane. This is followed by showing the binarized PXCT volume, which is the first step to segment the ensemble of particles. Then the manually drawn markers are shown, which are in the subsequent step used in the marker-based watershed segmentation to segment the entire ensemble into 434 fully imaged particles that aren’t cut-off by the field-of-view.

Movie S2:
A particle that portrays a weak degree of catalyst framework fragmentation ($V_r$ sorting ID = 3) is shown in 3-D as a maximum intensity projection of the 4 $k$-means clusters ($K_1$ is light blue, $K_2$ is light green, $K_3$ is orange, $K_4$ is red).
Movie S3:
A particle that portrays a moderate degree of catalyst framework fragmentation (V, sorting ID = 261) is shown in 3-D as a maximum intensity projection of the 4 $k$-means clusters ($K_1$ is light blue, $K_2$ is light green, $K_3$ is orange, $K_4$ is red).

Movie S4:
A particle that portrays a strong degree of catalyst framework fragmentation (V, sorting ID = 434) is shown in 3-D as a maximum intensity projection of the 4 $k$-means clusters ($K_1$ is light blue, $K_2$ is light green, $K_3$ is orange, $K_4$ is red).

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