A three-dimensional view of structural changes caused by deactivation of fluid catalytic cracking catalysts

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Since its commercial introduction three-quarters of a century ago, fluid catalytic cracking has been one of the most important conversion processes in the petroleum industry. In this process, porous composites composed of zeolite and clay crack the heavy fractions in crude oil into transportation fuel and petrochemical feedstocks. Yet, over time the catalytic activity of these composite particles decreases. Here, we report on ptychographic tomography, diffraction, and fluorescence tomography, as well as electron microscopy measurements, which elucidate the structural changes that lead to catalyst deactivation. In combination, these measurements reveal zeolite amorphization and distinct structural changes on the particle exterior as the driving forces behind catalyst deactivation. Amorphization of zeolites, in particular, close to the particle exterior, results in a reduction of catalytic capacity. A concretion of the outermost particle layer into a dense amorphous silica-alumina shell further reduces the mass transport to the active sites within the composite.

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In the process of fluid catalytic cracking (FCC), porous composites of zeolites and clay are used to transform heavy oil fractions into transportation fuels and petrochemical feedstocks. Over time these composites decrease in catalytic activity. Since this century-old process provides the majority of the world’s gasoline, there is a constant interest to prolong the lifetime and improve the performance of these composites.

Common FCC catalysts are spherical composites, 50–150 μm in diameter, formed by spray drying. They are composed of ~15–50% rare earth-stabilized (e.g., lanthanum) Y-type zeolite, a crystalline aluminosilicate, a functional matrix of calcined kaolinitic clay, an amorphous aluminosilicate, which may contain minor quantities of impurities such as TiO₂, and a binder composed of alumina and/or silica. This composition allows the composites to withstand operational conditions, while it also allows for the generation of hierarchical porosity. The composites contain an interconnected network of macro- (>50 nm), meso- (2–50 nm), and micropores (<2 nm), which ensures that feed molecules of various sizes experience a retention time in the composite sufficient for conversion into the desired products but brief enough to minimize overcracking.

During FCC unit operation, these composites are exposed to rapidly cycling temperatures. They are brought into contact with preheated feed at the bottom of the riser. During their ascent, cracking occurs at about 550 °C on active sites located on the surfaces of the functional matrix and, majorly, the microporous zeolites. A cyclone then isolates the composites from the products and transfers them to a regenerator. In the regenerator coke deposits, i.e., unreacted carbonaceous feed remnants, which cause a transitory deactivation of the catalyst are burned off at about 750 °C. The regenerated composites are returned to the riser, and the process repeats.

The permanent deactivation of FCC catalysts has been under extensive study over the last decades. Previous studies identified persistent coke deposits, the reaction environment in the riser, the hydrothermal conditions imposed by the regenerator, and feed contaminants, including sodium, nickel, calcium, vanadium, and iron, interacting with and accumulating in the composite as the main reasons behind permanent catalyst deactivation. The deactivation of the active zeolites itself through operational wear and impurities is now well considered, and zeolites are now designed to account for some material deactivation. However, the loss of zeolites through amorphization during operation, including aspects such as framework collapse and destruction, still remains one of the major expressions of catalyst deactivation. Because catalytic activity is presumed to be directly linked to pore size distributions (PSD), pore surface area, and zeolite accessibility, investigations now focus on changes to the support structure as well. Correspondingly, the pore network architecture is currently a topic of particular interest.

Structural changes within single composites, and thus structural contributions to the composites’ deactivation, can now be imaged by state-of-the-art microscopy. Having visualized an iron-enriched phase exclusively on the exterior surface of deactivated composites, Yaluris et al. suggested these changes to be a result of impurity uptake during operation and to contribute to catalyst deactivation. Based on the glassy appearance of these particles, they hypothesized an impurity-induced melting of binder and matrix components close to the particles exterior to be a reason for deactivation. Such a process would effectively reduce the number of macro- and mesopore openings on the particle exterior. Removal of these so-called diffusion highways, determining the flux of feed molecules to the zeolite domains, ultimately reduces the composite’s catalytic activity.

Martinez et al. extended these observations to other impurities, including nickel and the zeolite-poisoning vanadium and sodium. Structural studies of the pore network and the clogging of diffusion highways by metal-rich impurity deposits and, importantly, the pore network’s persistent integrity even after deactivation. Based on these observations, permanent catalyst deactivation is currently postulated to arise in part from the obstruction or removal of diffusion highways close to the particle exterior.

Here, we provide an updated view of FCC catalysts and the structural changes that lead to their deactivation. Quantitative ptychographic X-ray computed tomography of a pristine and of two industrial composites obtained from two FCC units operating at increasing severity of catalyst deactivation allows the visualization of differences in porosity and the localization of zeolite, amorphous silica–alumina (ASA), and clay components down to an isotropic resolution of ~35 nm. Independent of deactivation degree, clay/ASA elements are found to be enriched in the outer layer of the composite. In the case of the deactivated composites, we find that this layer, still containing pores and zeolite, condenses and forms a progressively non-porous ASA shell. The formation and growth of this shell thereby effectively isolates the composite’s interior from the reaction environment. These observations suggest FCC deactivation to be caused by a combination of zeolite amorphization, which reduces the catalytic capacity of a composite, and the concretion of the outermost composite layer into an isolating shell, which hinders the mass transport into and out of a composite.

Fig. 1 Electron micrographs of FCC catalysts. Shown are scanning electron micrographs of an FCC1, FCC2, and FCC3 particle. Highlighted is the morphological transition with catalytic deactivation. Scale bars are 10 μm.
Results

Bulk characteristics of fluid catalytic cracking catalysts. Pristine (FCC1) and commercially deactivated FCC catalysts (FCC2 and FCC3), manufactured under identical conditions, were provided by W. R. Grace Refining Technologies. Deactivated catalysts were retrieved from two industrial FCC units operating at increasing severity of catalyst deactivation. The extracted particles were subjected to a final calcination event. A fraction of these calcined particles extracted from the more destructive unit, FCC3, intended for tomography studies was further subjected to a cracking event in order to observe the state of a FCC particle leaving the riser.

Presented in Fig. 1 are electron micrographs of characteristic FCC particles after synthesis and as extracted from their respective units. Particles of FCC1 measure on average 76 µm in diameter, FCC2 74 µm, and FCC3 91 µm. With progressing deactivation, the initially smooth-surfaced and surface-porous particles undergo a gradual textural transformation and develop a surface comprised of nodules and valleys, resembling surfaces created by localized melt and vitrification events. Compositional analysis by means of inductively coupled plasma emission spectrometry revealed a total alumina concentration of ~50 wt.%. The unit cell of FCC1 was determined to be 2.451 nm, while the unit cell of FCC2 (2.429 nm) and FCC3 (2.430 nm) was virtually undistinguishable (Supplementary Table 1). The FCC3 particles, however, accumulated significant amounts of iron into this new surface morphology (Supplementary Fig. 1). The average iron concentration of FCC1, FCC2, and FCC3 particles is on the basis of Fe₂O₃ about 0.5, 0.7, and 1.6 wt.% respectively. Due to the presence of natural iron impurities in clay, around 0.5 wt.% Fe₂O₃ is expected for pristine particles. Compared to FCC1, both FCC2 and FCC3 have lower specific surface areas (FCC1 264 m² g⁻¹; FCC2 135 m² g⁻¹; FCC3 118 m² g⁻¹) and a reduced catalytic activity, as measured by conversion values of ~88, ~64, and ~56 wt.%, respectively. The loss of nitrogen-accessible surface area determined via physisorption (Brunauer-Emmett-Teller theory (BET)) is due to a decrease in available zeolite domains (157 to 82 to 50 m² g⁻¹) as for FCC3, this decrease is slightly offset by an increase in mesoporous surface area (107 to 53 to 68 m² g⁻¹).

Ptychographic X-ray computed tomography. To clarify the nature of these morphological and microstructural changes essential to the catalytic activity of FCC particles, we investigated one particle from each ensemble using ptychographic X-ray computed tomography, a technique capable of providing highly resolved quantitative 3D density maps. The individual particles were transferred onto tomography pins and without any further sample preparation, we imaged approximately one-third of each particle (Fig. 2). Derived PSD estimates are constrained by image resolution, which was estimated to be better than 31 (FCC1), 44 nm (FCC2), and 35 nm (FCC3) (Supplementary Fig. 2). In comparison with mercury intrusion porosimetry and literature reported BET-derived PSD, such resolution allows us to probe ~90% of the total macro- and mesopore volume (See Supplementary Fig. 3 and Methods for further information).

In the tomograms shown in Fig. 2, the individual composite components can clearly be distinguished. In order of decreasing electron density, these are particulates of titania, lamellar clay, globular zeolite, and a connected network of macro- and mesopores. Two distinct differences between the measured samples are apparent. While the pristine catalyst, FCC1, possesses numerous macropores that directly connect the particle interior with the exterior, the number of such diffusion highways (shaded pink area in Fig. 2) is found significantly decreased in the deactivated particle FCC2 or totally absent in FCC3. Instead of these pores, we find the exterior surface of FCC3 covered by an apparently non-porous shell indicated by a blue cross. The thickness of this shell is 1.4 ± 0.5 µm. Second, we are able to observe hydrocarbon deposits composed of coke and residual feed, red triangle, within the pore space of FCC3.

Plotted in Fig. 3a are electron density histograms of the FCC1 (i), FCC2 (ii), and FCC3 (iii) tomograms in their entirety, alongside histograms of individual composite components such

Fig. 2 Ptychographic image reconstructions. a Volume reconstructions of FCC1, FCC2, and FCC3. Orthoslices through the retrieved electron density maps are shown in b–d, respectively. Presented are bottom up (z-x) and orthogonal views (y-z, y-x). Cutting planes are represented by dotted lines. Shown in e-g are enlarged versions of selected areas. Common to all subfigures is the linear grey scale for the electron density. Selected diffusion highways (-) are highlighted in pink, hydrocarbon deposits by a red triangle, and the ASA shell by a blue cross. Voxel size is about (20 nm)³. Scale bars are 5 µm.
as zeolite. From Fig. 3a (iii) we observe the calcined clay, essentially an amorphous mixture of alumina and silica, and the iron-enriched ASA shell\textsuperscript{14} to possess identical electron densities. Further, a large fraction of zeolites throughout the particle seem to accumulate smaller mesopores with deactivation leading to a shift toward a lighter electron density (Fig. 3a (i and ii); Fig. 2b–d). This shift is a result of partial-volume effects, i.e., the mixture of multiple components in a single voxel. The progressing deactivation leads then to the formation of ASA, and the split peak observed in Fig. 3a (iii).

Tomograms were segmented into the three elementary constituents of a FCC particle, pores, zeolite, and clay/ASA, by assigning each identified component to one of these constituents (Fig. 3a (iv)). Because of the colocalization of hydrocarbons and...
air within the pore network, we assigned air and hydrocarbons to pores. Titania was assigned to clay/ASA, being natural to the composites functional matrix. In general, we observe these three elementary constituents to be well dispersed (Fig. 3b–d). For instance, we determined the intra-particle distances of clay/ASA and zeolite, and the grouped clay/ASA fraction. The center of the extracted sub-volume is equal to 0 and the exterior surface is equal to 1. Plotted in b–d are the volumetric compositions of FCC1, FCC2, and FCC3, respectively. Highlighted in blue is a projected shell region ~1.5 μm in thickness contains major amounts of zeolites, which are largely absent in FCC3, see also distance maps of clay/ASA and zeolite (Fig. 3e, f).

The segmented tomograms can further be used to approximate the volumetric composition of each composite (Supplementary Table 1). Overall FCC1, FCC2, and FCC3 possess similar volume fractions of pores, ~23 vol.% of zeolite, ~53 vol.% and clay, ~24 vol.% (Supplementary Table 1). To assess the spatial distribution of components, we analyzed individual subvolumes, radiating from the core of the composite to the exterior, with regard to their volumetric composition (Fig. 4). Pores, zeolite, and clay/ASA are homogeneously distributed throughout FCC1 and FCC2. The outer shell region is composed of ~20 vol.% pores, ~55 vol.% zeolite, and ~25 vol.% clay/ASA. The porosity of FCC3 drops continuously toward the particle exterior (~38 to ~1 vol.%), as does the volume of identified zeolites. The two outermost micrometers in FCC3 are composed of ~77 vol.% ASA and ~21 vol.% zeolite.

In order to establish a connection between individual particle observations and their parent populations, we calculated the specific surface area of detectable macro- and mesopores in the tomograms. The specific surface area for FCC1 is ~132 m² g⁻¹, ~80 m² g⁻¹ for FCC2 and ~92 m² g⁻¹ in the case of FCC3. These specific surface areas exceed by far the BET-determined surface areas of the parent populations, namely 107, 56, and 68 m² g⁻¹. Since, unlike sorption experiments, tomographic observations are independent of access to the reaction environment. This difference can be a result of pores isolated from the reaction environment. Assuming that the tomographically sampled particles provide a good representation of the population average, this suggests that independent of deactivation degree up to 30 % of pores are not participating in mass transport.

This conclusion is supported by a detailed analysis of the pore networks in the tomograms of FCC1, FCC2, and FCC3, which reveals the existence of a multitude of minor disjointed networks and one interconnected network accounting for ~80 vol.% of the pores. Shown in Fig. 5a–f are calculated thickness maps of the interconnected pore networks. Here each porous region is fitted with maximal spheres, which fill this region best thereby creating a pore diameter map. Volume reconstructions are presented in the Supplementary Movies 1–3. PSD derived from thickness maps (Fig. 5g) reveal no substantial differences between deactivated samples. Both FCC2 and FCC3 possess a narrow PSD centering at 70 nm. In contrast, FCC1 possesses a much wider PSD whose majority is confined within the range of 30–300 nm. The fraction of pores smaller than 100 nm in diameter is in part magnified by irregular pore surfaces best fitted with a number of small spheres and pore throats connecting individual pockets (Fig. 5d–f). Comparing the PSD of the pristine sample, FCC1, to the deactivated sample FCC2 and in particular to FCC3, we observed a shift toward larger pores in agreement with the formation of macropores >3 μm detected in Fig. 3.

Plotted in Fig. 5h is the ratio of detectable macro- (>50 nm) and mesopores (<50 nm) as a function of fractional distance to the particle exterior, revealing a homogenous distribution of macro- and mesopores within FCC1 and FCC2, slightly increasing in mesopores when approaching exterior surface for FCC2. In FCC3 we observe a sharp drop in macropores and a respective increase in mesopores as we move to the exterior surface. Figure 5h further highlights the increased fraction of detectable mesopores in FCC1. Considering the equal pore volumes across all tomograms and the increased measurable surface area of FCC1, this iterates the existence of a finer, i.e., a spatially thinner pore network in FCC1.

These pore networks ultimately determine how effectively zeolite domains within the particle are utilized during operation.
We therefore aimed to quantify the diffusion highways entrance cross section, for FCC1 we estimated their entrance area to be <5% of the particle exterior surface area. For FCC2 we find only ~1%. Furthermore, the individual entrances rapidly narrow to <150 nm in diameter as we move into the particle. No such connections could be found in the FCC3 tomogram. Rather, we find the pore network to be isolated from the exterior by the dense outer shell on the observable length scale (Supplementary Movies 1–3).

When estimating the theoretical catalytic capacity by the measurable interfacial area of zeolite domains in contact with the reaction environment, including the particle exterior surface and the pore space but disregarding zeolite micropores and composite elements, which appear isolated because of limited image resolution and field of view, about 70% of the total measurable zeolite surface area can be utilized in FCC1 and circa 60% in both FCC2 and FCC3. Whereas in FCC1 and FCC2 ~10% of this surface area is contributed by zeolites located on the particle exterior, this number is below 2% in FCC3 (Supplementary Table 1).

**X-ray fluorescence and X-ray diffraction tomography.** To query this loss of exterior facing zeolites further, we investigated an
Examination of the parent populations of pristine and FCC catalysts at increasing severity of deactivation revealed little difference in elemental composition or zeolite unit cell dimension. However, our measurements indicate a significant decrease in specific surface area and functional zeolites. Approximately 50–70% of the active microporous area is lost to zeolite amorphization in the deactivated samples. Still, FCC2 and FCC3 particles retained ~73% or ~64%, respectively, of their original catalytic capacity. Our X-ray tomography study of structural changes on the single-particle level provides some insight into the overarching catalyst deactivation behavior.

We observe a shift from the pristine sample toward an initially less electron dense arrangement and, with progressing deactivation, to a subsequently more dense arrangement (Fig. 3a (i–iii)). This trend is in agreement with a progressing zeolite amorphization including zeolite internal mesopore formation, visible throughout the particle (Fig. 2b–d) and ASA development following.

Segmented tomograms reveal a nominally unchanged composition across the examined particles. While a distinct change of the internal structure between the pristine and the deactivated samples is detectable, including a shift toward larger pores and a concurrent decrease in specific surface area, we found no structural changes that lead to a decrease in catalytic activity between the deactivated samples. Rather, we observe the more deactivated sample to possess a slightly increased pore volume, macro- and mesoporous surface area and network connectivity, offsetting the effect of progressing zeolite amorphization with regard to catalytic activity. Similarly, the analyzed particles possess near identical interfacial areas of feed-transporting pores with zeolite elements. If such global metrics were applicable, both samples should possess a similar functional capacity.

We therefore conclude that the observed drop in catalytic activity is not solely due to the loss of functional zeolites but also a result of localized changes, i.e., to the particle exterior surface. While these changes are not readily detectable by common characterization methods such as Powder-XRD and BET, they are responsible for a drastic reduction of both active sites on the particle exterior surface and accessibility of active sites within the composite.

Others already suggested that macroscopically measurable structural metrics do not accurately describe the diffusion...
limitations in or the catalytic performance of FCC particles and that diffusion coefficients, e.g., present a more accurate picture. Wallenstein et al. reported diffusion coefficients in the range of $10^{-2} \text{ to } 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which suggest that intra-particle diffusion in FCC particles occurs predominantly within pores of $\sim 100 \text{ nm}$ in diameter, the so-called Knudsen regime. Correspondingly, the tomograms presented here register numerous pore throats of the size of voxels within the interconnected pore networks. The major pore network in FCC1, FCC2, and FCC3 was found to contain numerous transport-limiting pore throats, suggesting no significant differences in intra-particle diffusion (Supplementary Movies 1–3). Further, an estimated 1D diffusion length of 140–1400 $\mu \text{m}$ per reaction cycle would indicate that feed molecules have access to all available active sites independent of their distance to the particle exterior.

However, the morphological appearance of the FCC particles changes considerably with increasing deactivation. Particle collisions in the fluidized bed reactor cause smaller particles to fragment and cause surface abrasion. Attrition-created collisions in the active sites independent of their distance to the particle exterior. Assuming a spherical particle with radius of 40 $\mu \text{m}$, the shortest distance and biggest cross section to the feed stream, they only do these zeolites represent the active components with the highlighted as particularly relevant for catalytic behavior. Not the results provide a complementary explanation to the common further the mass transport in and out of the composite. These distinct ways. The amorphization of zeolites within and on the exterior surface into an amorphous mixture of silica and alumina combining with adjacent clay elements would then facilitate the observed ASA shell formation. The detection of a shell around FCC2 and to a lesser extent around FCC1 even though porous and zeolite containing points to the catalyst synthesis itself and a gradual formation process occurring over a set number of reaction cycles as possible origins of shell formation. The actual concretion of the shell and the inherent reduction in diffusion highways leads then to a reduction in catalytic activity. The amorphization of zeolite crystals close to the exterior surface into an amorphous mixture of silica and alumina combining with adjacent clay elements would then facilitate the observed ASA shell formation. The FCC catalyst population based on differences in skeletal density. Commercial FCC catalysts may contain several additive particles, which are used to control SO$_x$ emission, to improve octane or to reduce sulfur quantities in gasoline. The sink/float method effectively removes these additives from the cracking catalyst of interest. We imaged one pristine FCC particle (FCC1), one extracted from an industrial unit with a low amount of catalyst deactivation due to iron impurities (FCC2), and one extracted from a unit at the far end of the spectrum (FCC3). All samples had the same starting formulation. They are composed of USY type zeolite, which had been cation-exchanged to 8% lanthanum oxide, kaolin clay, and a silica and alumina binder. The FCC3 particle, which was to be imaged via ptychography, had further been subjected to a cracking experiment. This resulted in a coke sample, simulating the state of an FCC particle leaving the riser/stripper. Chemical composition and selected physical properties are given in Supplementary Table 1. Surface area, mercury intrusion porosimetry, and electron microscopy analysis were conducted on calcined FCC particles to ensure comparable results.

**Electron microscopy.** Scanning electron micrographs were acquired using either a 5400 Hitachi FSEM or with a Quanta Q200 operated at 20 $\text{keV}$. The samples were coated with 5 nm of Pt/Pd. For transmission electron microscopy, FCC particles were first embedded in epoxy resin, and the obtained cylindrical blocks were then polished and cut into fine slices. For scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDXS) investigations, these slices were further mechanically thinned and coated ion-milled. High-angle annular dark-field STEM micrographs and EDXS were acquired using either a Hitachi HD 2700CS or with a FEI Talos microscope, both operated at 200 $\text{keV}$.

**FCC catalyst composition.** Chemical composition of FCC catalysts was determined by an inductively coupled plasma technique.

**Powder-XRD.** Powder-XRD measurements were performed using a Bruker D8 Advanced diffractometer equipped with a CuK$\alpha$ X-ray source.

**Surface area determination.** The surface area of FCC catalyst particles was determined by nitrogen physisorption, using a Micromeritics Tristar 3000. Prior to each measurement the sample was degassed at 300 $\text{°C}$ for 10 h. The r-plot method was used to determine the individual contributions of zeolite and matrix to the total surface area.

**Mercury intrusion porosimetry.** Mercury PSD measurements were carried out using a Micromeritics Autopore IV 9520 unit. The sample was pre-treated at 200 $\text{°C}$ for 15 min, then at 540 $\text{°C}$ for 1 h. About 0.5 g of the sample was loaded into a 3 ml powder penetrometer. The mercury intrusion pressure was increased in a stepwise manner from 0.1 to 60,000 psi. The volume of mercury intruded after each step is measured and recorded. Acknowledging the unreliability of MIP regarding the analysis of pores with irregular shapes, the pore diameter was calculated using the Washburn equation with a contact angle of 140°.

**X-ray fluorescence and X-ray diffraction tomography.** Simultaneous microbeam diffraction (µXRD) and microbeam fluorescence (µXRF) tomography experiments were carried out at the microXAS beamline of the Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland. A 17.3 $\text{keV}$ incident pencil beam was focused with a Kirkpatrick–Baez (KB) mirror system to a size of 1.5 $\times$ 1.5 ($\text{H} \times \text{V}$) $\mu \text{m}$. For X-ray fluorescence tomography, diffraction patterns collected from Al$_2$O$_3$ polycrystals were used to calibrate the sample-to-detector distance. The detector, a DECTRIS PILATUS 100 K, was positioned about 5 cm from the sample. Measured diffraction patterns were integrated using the integration software XRDUA. For microbeam X-ray fluorescence, XRF spectra were collected using a Si drift diode detector (Rigaku) and fitted using Pyle.$^15$ To conduct tomography experiments, we glued a single FCC particle on top of a tomography pin using UV-curable resin. After aligning the tomography pin with the sample stage’s center of rotation, we simultaneously recorded both XRD patterns and XRF spectra at 91 sample positions with a step size of 1 $\mu \text{m}$ across 141 projection angles, equally spaced by 2°. A total of 16,471 diffraction patterns were collected. The one-dimensional diffraction patterns obtained by Azimuthal integration were then analyzed as a function of position and rotation to construct one sinogram per 2$\theta$ value, generating a total of ~5000 sinograms covering a total range of 1.5–56° in 20 with a step size of $\sim 0.01^\circ$. Using these sinograms, a simultaneous iterative reconstruction technique (SIRT) algorithm was applied. Acquired XRF spectra were analyzed in similar fashion, constructing a single sinogram per XRF intensity. This resulted in ~1600 sinograms, covering a total range of 2–18 $\text{keV}$ with an energy resolution of $\sim 130 \text{ eV}$. The procedure detailed above allowed us to obtain the full XRF spectrum and the full powder-XRD pattern per voxel of the topographically reconstructed volume. We collected tomographic data for three equally spaced slices, each 1.5 $\mu \text{m}$ in height, across the center of the particle. One of these slices is shown in Fig. 6.

**Methods**

**Materials.** A pristine and two commercially deactivated FCC catalyst (Ecat) samples, manufactured under identical conditions, were provided by W. R. Grace Refining Technologies. The deactivated FCC particles were extracted from two industrial FCC units. The isolated particles were then digested to remove any residual coke deposits and separated using a sink/float method, which sorts the FCC catalyst population based on differences in skeletal density. Commercial FCC catalysts may contain several additive particles, which are used to control SO$_x$ emission, to improve octane or to reduce sulfur quantities in gasoline. The
**Data availability**

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

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Author contributions
J.I., R.R.J., M.H., M.G.S., A.D., and J.C.d.S. performed ptychographic X-ray computed tomography experiments. J.I., R.R.J., D.F.S., J.I., and D.G. collected and processed pXRF and µXRD data. W.C.C. and Y.Y.S. conducted EMPA, Hg porosity, and BET experiments. R.R.J., F.K., W.C.C., and Y.Y.S. performed EM experiments. J.I. analyzed data and wrote the manuscript. A.M. and J.A.v.B. conceived and led the project, gave conceptual advice, and edited the manuscript. All authors read and approved the manuscript.

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