Resonant Ptychographic Tomography Facilitates Three-Dimensional Quantitative Colocalization of Catalyst Components and Chemical Elements

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Abstract:

The ability to localize selected chemical elements within individual components of functional matter is of great value to our understanding of material behavior. By means of resonant ptychographic X-ray computed tomography, we here provide such colocalization information with nanoscopic spatial resolution. Spatially correlated quantitative tomograms of electron density and iron concentration allowed the localization of native and feedstock-introduced iron impurities within the primary components of a prominent heterogeneous catalyst. Examinations found no direct evidence in favor of the currently suggested impurity-driven deactivation mechanisms of fluid catalytic cracking catalysts. The majority of iron impurities, present in the form of nanosized magnetite particulates, are found embedded in the outermost layer of an otherwise, iron-poor, particle isolating amorphous silica-alumina envelope. Observations query both deactivation driven by impurity pore clogging and iron-impurity induced melting of catalyst components. The presented approach is general, extendable to secondary impurities or materials and spectroscopic ptychographic tomography. Future applications such as active-site localization and speciation in heterogeneous catalysis are envisioned.
Introduction:

The ability to colocalize chemical elements with selected features of functional matter is vital to improve our understanding of material behaviour. Resonant ptychographic X-ray computed tomography (R-PXCT) promises to provide such quantitative colocalization information in 3D at unprecedented spatial resolution. We here show its applicability towards the examination of a functional material, fluid catalytic cracking catalysts.

Fluid catalytic cracking (FCC) refers to a chemical conversion process that provides the majority of the world's gasoline. To this end, catalyst particles of hierarchical porosity are used to crack the heavy fractions in crude oil. Pristine particles are composed of La-exchanged Y-type zeolite and calcined kaolinitic clay naturally rich in iron. The catalytic activity of FCC catalysts decreases during long-term industrial operation. This decrease in catalytic activity enforces a continuous replacement of catalyst particles, resulting in an annual demand of around 620 kilo tons worldwide.

Studies identified the harsh reaction environment in the FCC unit, i.e. a hydrothermal environment with temperatures up to 800°C, as well as the interaction with and the uptake of feed contaminants, especially iron, as potential origins of this permanent deactivation. Deactivation itself is postulated to be a result of two processes. A progressing amorphization of zeolites, including micropore collapse and mesopore formation, leading to a decay in the number of active sites and the clogging/elimination of particle-exterior-connecting pores leading to a reduced flux to the active sites within the composite. The removal of particle-exterior-connecting pores has received two possible explanations thus far.
On one hand and on the basis of comparably low-resolution X-ray tomography studies it was suggested that this loss of pores and flux is in part due to the obstruction of pores by iron-rich impurity deposits. On the other based on scanning electron microscopy of industrially spent catalysts, uncovering an iron-rich particle isolating amorphous silica-alumina (ASA) envelope, it was suggested that the incorporation of feedstock impurities leads to an impurity induced phase transformation process, i.e. melting, of the outermost catalyst particle layer.

We report on a three-dimensional colocalization study of native and feedstock-introduced iron impurities with the primary components of a deactivated FCC catalyst, which failed to confirm either explanation at the attained spatial resolution of 39 nm. While feedstock-introduced iron impurities are found in a continuous, catalyst-isolating amorphous silica-alumina envelope, the embedded iron herein is found majorly in the form of iron oxide nanoparticles sitting in confined areas on the particle exterior surface. No major colocalization between present pore throats and substantial iron deposits could be observed. Observations are suggestive of an inwards directed growth of the ASA envelope. Further, observed was a positive correlation of increased zeolite mesoporosity with iron concentration beyond the spatial extent of the isolating envelope. Overall zeolite domains appear to be affected by FCC unit operation, showing increased levels of mesoporosity and or increased packing density, suggestive of a progressing impurity or steaming-induced zeolite amorphization process regardless of the level of incorporated iron impurities.
Results:

FCC catalysts, roughly 100 µm in diameter, were extracted from an industrial FCC unit operating at a severe level of catalyst deactivation. Catalysts show on average a 25% decrease in catalytic activity, a concurrent 64% decrease in micropore volume and a fourfold increase in iron concentration (~2.53 wt.%) compared to pristine catalysts (~0.5 wt.% FeO), Supporting Table 1. A sixth of a catalyst particle was imaged using Fe K-edge R-PXCT. Experimental details are provided in the method sections.

In short, ptychographic phase tomograms acquired away from X-ray absorption edges are quantitative in regard to electron density and hence allow 3D compositional analysis, e.g. the identification of catalyst components. Due to anomalous scattering effects, tomograms acquired at absorption edges or resonance energies exhibit a chemical sensitivity in areas that include the edge-specific element. Differences between off- and on-resonance acquired tomograms can therefore be used to determine the location and concentration of the element. A priori knowledge from independent spectroscopic measurements indicates that the average Fe K-edge energy of a deactivated FCC particle lies for more than 95 % of the present iron impurities within ±2 eV of the selected resonant measurement energy, 7123 eV. Thus, a subtraction of spatially registered off- and on-resonance tomograms, considering differences in scattering factor, provides a quantitative iron distribution tomogram at a spatial resolution of the acquired electron density tomogram, here 39 nm with an inherent uncertainty in iron concentration of ~3 %, Supporting Figures 1-3. The achieved resolution is suitable to probe around 85% of the occluded meso- and macropores when compared to mercury intrusion
porosimetry (MIP) determined pore size/pore volume distribution, Supporting Figure 4.19

Presented in Figure 1 are orthoslices (a-b) through and volume rendering(s) (c-d) of the obtained electron density and iron concentration tomograms alongside their corresponding histograms (e-f). Figure 1a, visible in the electron density tomogram are the main catalyst components, an interconnected pore-network of meso- and macropores, granular zeolite and fibrous clay.19, 29 Moreover, apparent is the inhomogeneous distribution of these components. Pore and zeolite fractions decrease gradually in frequency towards the particle exterior where the ASA envelope is prevalent. This envelope possesses a rather uniform thickness of 1 to 2 µm and sharp transition to the particle interior. With few exceptions, this envelope isolates, on the observable length scale, the catalyst from the exterior.

Figure 1b, iron impurities are found sparsely dispersed throughout the entire particle, accumulating in zeolite and clay domains as well as in the ASA envelope. The iron concentration, henceforth expressed in terms of iron atoms per cubic Ångström, is in the majority of these areas significantly less than 0.01 n_{Fe Å^-3} or well below the concentration of iron silicates. Some voxels do however possess iron concentrations up to 0.04 n_{Fe Å^-3}, equal to iron oxide particles. The majority of voxel, possessing iron concentrations greater than 0.02 n_{Fe Å^-3} are found clustered in isolated areas either in the outermost layer of the ASA envelope or on top of the particle exterior surface. Figure 1 c-d, these surface deposits, showing correspondingly increased values of electron density, match overall well in location and appearance with previously reported surface nodules.16 A comparison of measured iron concentrations and electron densities in these nodules with those of reference
compounds, Supporting Table 2, is suggestive of spatially unresolved iron particulates mixing with catalyst components on the single-voxel level. Surprisingly, a fraction of the present nodules do not show increased iron levels, nor do elevated iron concentration in the ASA envelope necessarily correlate with the spatial extent or apparent packing density hotspots of the ASA envelope itself.
Figure 1: Resonant Fe K-Edge Ptychographic Tomography of a Deactivated Fluid Catalytic Cracking Catalyst. Provided are orthoslices through the measured electron density tomogram (a) and iron distribution (b). An enlarged version of a selected area highlighting a particle exterior connecting pore (pink) is given (turquoise rectangle). Presented are bottom up, top down (z-x) and orthogonal views (y-z, y-x). Orthoslice cutting planes are represented by the dotted lines. (c) and (d) volume rendering of electron density and iron distribution tomograms. Scale bars common to all orthoslices and volume renderings are 5 µm. The electron density tomogram is based on the off Fe K-edge phase tomogram acquired at 7.310 keV. The presented iron distribution was derived from the
difference between off and on, 7.123 keV, Fe K-edge phase tomograms. Fourier shell correlation implies a half-period spatial resolution of (39 nm)$^3$ in both on- and off-resonance measurements. Electron density and iron concentration histograms are shown in (e) and (f), respectively. Electron densities and iron concentrations of known catalyst components and reference compounds are provided. Further given are histograms of isolated volumes (~300 nm)$^3$ of air located outside of the particle providing an uncertainty estimate of both electron density and iron concentration. The full width half maximum (FWHM) in case of the electron density histogram is 0.05 n$_e$Å$^{-3}$. For the iron distribution, the FWHM is 0.003 n$_{Fe}$Å$^{-3}$.
Shown in Figure 2a are orthoslices through and a volume rendering of the threshold-segmented electron density tomogram isolating the main catalyst components. Threshold levels were chosen based on electron densities of known catalyst components. Clay and ASA domains were grouped due to similar electron densities. The segmented tomogram reiterates the inhomogeneous distribution of catalyst components. Looking at the particle exterior, observable is a limited number of particle-exterior-connecting pores, reduced zeolite domain size and frequency when compared to the particle interior or the exterior of a pristine FCC catalyst. Ensuing segmentation, a radially averaged analysis of composition was conducted. Reported are distance averaged changes in composition, electron density and iron concentration. Plotted in Figure 2b is the catalyst composition as a function of distance to the particle exterior. Observable is a sharp increase in clay/ASA towards and across the isolating catalyst envelope, concurrent with a decrease in pore and zeolite concentration.

Plotted in Figure 2c is the mean electron-density of the entire catalyst and of volumes segmented as clay/ASA and zeolite domains as a function of distance to the particle exterior. Additionally, provided is the average electron density of these components as measured in a pristine FCC catalyst. The electron density in the presented line plots shows a common profile for the entire catalyst and the clay/ASA domains. This profile compromises a plateau up to ~1500 nm from the particle exterior, a sharp increase in electron density, concurrent with the detection and spatial extent of the ASA envelope and an ill-defined second plateau starting from around 500 nm up to the particle exterior. The deactivated catalyst averaged electron density is slightly lower compared to the
pristine catalyst in the core area. This is potentially a result of synthesis differences or FCC-unit-operation induced changes. Within the spatial extent of the ASA envelop the overall electron density, expressed in terms of electrons per cubic Ångström, nearly doubles from 0.40 to 0.75 n_\text{e}\text{Å}^{-3}. Changes in the electron density of the clay/ASA domains provide an explanation for this overall increase in electron density. For the clay/ASA domains, an increase in electron density from 0.63 n_\text{e}\text{Å}^{-3} in the core area up to 0.78 n_\text{e}\text{Å}^{-3} in the outer envelope is observed. The latter is similar to the expected electron density of the thermal phase transformation products of kaolinitic clay such as metakaolin (0.73 n_\text{e}\text{Å}^{-3}). Importantly, there exists a discrepancy between theoretical electron density values of the fibrous calcined clay and the measured electron density in the core area (0.73 compared to 0.63 n_\text{e}\text{Å}^{-3}). This discrepancy can be explained by partial-volume effects, e.g. spatially unresolved pores on a single voxel level. Formation of the ASA envelope during unit operation alleviates this spatial resolution limitation, due to an increased packing density in this area and the concurrent elimination of unresolved pores. In total, this leads to retrieved electron density values matching theoretical values in this selected region.

A similar reasoning applies to the observed discrepancy between the measured electron density of the microporous zeolite and its theoretically expected density (~0.44 compared to ~0.58 n_\text{e}\text{Å}^{-3}). Observed in the radial electron density profile of segmented zeolite, Figure 2c, is a gradual increase in electron density towards the particle exterior, from 0.41 to 0.49 n_\text{e}\text{Å}^{-3}. These extremes are both lower and higher, compared to the electron density of those of zeolites found in pristine FCC catalysts, Supporting Figure 5. The equivalent electron density inflection point is found roughly 1500 nm from the particle exterior or the spatial extent of the ASA.
envelope. These changes in zeolite electron density, given their microporous nature and the known tendencies of mesopore formation and structural collapse under steaming conditions, imply a substantial amount of framework collapse in zeolite domains occluded in the outermost particle envelope and a particle inwards directed decay in zeolite mesoporosity. To note is that segmented zeolite domains are identified based on their electron density, and thereby any significant structural changes such as transitions to mesoporous zeolite and/or to collapsed, amorphized zeolites will result potentially in a change in classification as pores or clay/ASA.

Plotted in Figure 2d is the average iron concentration of the entire catalyst, in clay/ASA and zeolite domains as a function of distance to the particle exterior. The overall iron concentration and the concentration in clay/ASA domains show a similar profile in the interior of the deactivated catalyst particle as well as inner parts of the ASA envelope, only the outermost ~500 nm show enhanced iron levels. The zeolite/iron profile shows an additional feature near the electron density inflection point. Observed is a minimal increase in iron concentration with increasing zeolite density.
Figure 2: Segmentation and Radial Analysis of Electron Density and Iron Concentration within a Deactivated FCC Catalyst. (a) Electron-density segmented tomogram of the imaged FCC catalyst, Figure 1a. Provided are orthoslices and volume render of the threshold segmented tomogram highlighting the distribution of the main catalyst components, pores (blue), zeolite (red) and clay/ASA (yellow). Cutting planes are represented by the dotted lines. Scale bars are 5 µm. Segmentation was initialized based on electron density intersections of visually pure and isolated catalyst components with volumes in the range of (250–300 nm)$^3$. (b) Radial distribution profiles of segmented catalyst components. Plotted is the catalyst composition as a function of distance to the particle exterior. Distances were calculated using a three dimensional distance map. (c) Radial changes in electron density of the entire particle, zeolite and clay/ASA domains. Plotted is the weighted mean and standard deviation. Electron density references are provided on the basis of pristine FCC catalyst measurements. (d) Radially averaged iron concentration in zeolite, clay/ASA domains and across the entire particle. Only iron deposits greater 40 nm in diameter and iron concentrations greater than 0.003 nFeÅ$^{-3}$ were considered. The dotted blue line in (c & d) stresses the transition point in zeolite electron density from mesoporous to zeolites potentially exhibiting framework collapse.
Construction of a bivariate histogram, **Figure 3a**, allows for the examination of specific colocalization events, the determination of colocalization degree and insight into the nature of occluded iron impurities through two-factor identification – electron density and iron concentration.

Two colocalization centers are visible in the bivariate histogram, corresponding to the native iron-rich clay and iron-enriched zeolites in the particle core. The iron concentration in clay domains readily matches those expected between 0.001 and 0.005 n\textsubscript{Fe}Å\textsuperscript{-3}\textsuperscript{37}. Considering the determined noise threshold of roughly ~0.003 n\textsubscript{Fe}Å\textsuperscript{-3}, **Figure 1f**, only 10% of all voxel could be correlated. This leads to a particle overarching correlation degree between iron concentration and electron density of 0.14. Such a low correlation coefficient is well in agreement with the observed strong localization of iron impurities to isolated areas on the particle exterior, **Figure 1d**, and the expected total iron content of ~ 2.5 wt.% on the basis of iron oxide in the entire particle.

While a few selected voxel can directly be classified as iron oxide particles based on their electron density and iron concentration and are indeed dominantly located on the particle exterior, the nature of the vast majority of iron impurities remains elusive by this approach. Further insight, can be garnered from the shape of the bivariate histogram. Present correlative plume, in direction of increasing electron density and iron concentration, is indicative of spatially unresolved iron impurities. The majority of voxel included in this plume, determined by bivariate segmentation **Figure 3b**, are found located on the particle exterior or located in the outermost region of the ASA envelope. Further, extrapolation of the encountered electron density - iron concentration pair, considering present clay/ASA components, would lead to a
projected density-concentration pair of magnetite, hematite or ferrous oxide. In turn, suggesting that almost all iron within the ASA envelope is present in the form of iron oxide particulates smaller than ~15 nm in diameter. Transmission electron micrographs, energy-dispersive X-ray spectroscopy (EDXS) maps and electron diffraction of thinned ASA envelope sections were used to confirm this postulation, Figure 3c and Supporting Figure 6. Identifiable are magnetite particles on the order of 10 nm dispersed in the outermost layer of the otherwise amorphous iron poor and Si-rich ASA envelope. No iron silicate or aluminate particles could be detected. The acquired correlative information enables us equally to query the second postulated impurity-driven deactivation mechanism, namely the physical obstruction of pores by impurity deposits. To this task, we calculated a distance map between substantial iron deposits (those greater 0.005 nFeÅ⁻³ and (40 nm)³) and pore space. The obtained distribution was further filtered to isolate any substantial iron deposits in close proximity, <100 nm, to the pore space, Supporting Figure 7. Visual inspection of these deposits, potentially involved in the obstruction of pore throats, revealed them to be firmly located within the ASA envelope and associated with isolated pores therein. A colocalization of pores and iron deposits can as such be confirmed. However, only a single pore connection to the particle interior, marked in Figure 1a by a turquoise rectangle, could be detected which is potentially blocked by iron deposits and not cut-off by the ASA envelope at the attained spatial resolution. See also Supporting Movies.
Figure 3: Bivariate Histogram, Bivariate Segmentation and Electron Microscopy. (a) Bivariate histogram showing the correlation between iron concentration and electron density on a voxel level. The air outside the particle was masked and the scale limited to iron concentrations greater 0.003 \( n_{Fe} \text{Å}^{-3} \). Electron density and iron concentration of selected iron-rich reference components are given. The degree of correlation given by Pearson's correlation coefficient is represented using a color map, ranging from 0 (blue) to 1 (yellow). (b) Bivariate segmented voxels (blue) possessing both elevated electron density and iron concentration values (area in the histogram given by an orange rectangle) are shown overlaid onto the electron density. Presented is a bottom up orthoslice with the area indicated by a dashed orange rectangle enlarged below. Scale bars are 5 \( \mu \text{m} \). The histogram selected area is predominantly composed of voxels located within the ASA envelope or are located on the particle exterior. (c) Transmission electron micrograph and elemental X-ray spectroscopy maps of aluminium (red), silicon (green) and iron (blue) of a corresponding thinned catalyst section. Evident is the distribution of iron particles in the outermost ASA envelope layer. Scale bar is 80 nm. (d)
Electron micrograph at increased magnification and Fourier transform of a single iron particulate. Indexing of the obtained pattern identifies this particle to be of spinel structure e.g. magnetite. Scale bar is 2 nm. (c & d) Sections were taken from a randomly selected deactivated FCC catalyst at approximate equal positions given by the orange star and triangle.
**Discussion:**

Resonant ptychographic X-ray computed tomography revealed the colocalization of a selected element with physical features in a deactivated FCC catalyst at an unprecedented spatial resolution and field of view.

Our investigation revealed in a first instance a surprising inconsistency between zeolite microporosity loss and resulting reduced catalytic activity.\(^{19}\) Acquired electron density tomogram and the associated examination of occluded zeolite domains suggest this discrepancy, *i.e.* an unexpectedly high level of retained catalytic activity, to be a result of a radially progressing mesoporous zeolite formation past the isolating ASA envelope. Increased zeolite mesoporosity and the accompanying access to previously underutilized active sites within the individual zeolite domains may, to a certain degree, offset the loss in flux caused by the ASA envelope and total active site reduction due to amorphized zeolites.\(^{35, 36, 38}\)

Resonant Fe K-edge tomography provided iron concentration and electron density distributions that allowed us to clarify several aspects of potentially impurity-driven catalyst deactivation mechanisms. The colocalization of iron in zeolite domains of increased mesoporosity in the core of the particle and framework collapse in the ASA envelope could suggest a decrease in thermodynamic stability of zeolites as a result of iron incorporation.\(^{22, 39}\) This is not conclusive given that the majority of zeolites contain iron on the experimental noise level and show equally enhanced levels of mesoporosity. Therefore, present hydrothermal reaction conditions, secondary incorporated impurities such as calcium,\(^{26}\) and soluble, not incorporated, impurities have to be taken into consideration when discussing deactivation drivers and their significance.
The flux-limiting ASA particle envelope, suggested to have formed on the basis of impurity-induced low-temperature eutectics\(^\text{16}\) is demonstrated to contain iron in select and sparsely distributed volumes. However these regions do not exhibit significantly higher iron concentrations as found in the naturally iron-rich clay phase for the most part. Only the outermost layer shows consistently higher iron concentrations, e.g. on the order of iron silicates and/ or partially resolved iron oxide nanoparticles. Iron hotspots, an amalgamation of spinel type nanoparticles smaller than 15 nm, are found inhomogeneously deposited solely on the particle’s outer surface. Given the limited intrusion depth of these particulates, observations are in favour of an inwards directed growth of the ASA envelope, consisting of a progressing amorphization of clay and zeolite domains and their intermixture. The sharp transition between ASA envelope and particle core is no direct evidence for an outward directed growth. Bread crust structures of fixed thickness are common observation in materials exposed to the high temperature environments\(^\text{40, 41, 42}\) The role of embedded or structurally incorporated iron impurities in this process needs as such re-evaluation to determine whether they are the cause, spectator or catalyst of envelope formation\(^\text{43}\)

The failure to retrieve any substantial evidence of catalyst deactivation driven by impurity pore clogging should not be seen as total absence of the former\(^\text{9, 26}\). Spatial-resolution limits currently prevent us from evaluating potential occurrences of pore blocking at pore diameters smaller than ~40 nm. However considering the detection of an interconnected and divergent pore network\(^\text{19}\) at present spatial resolution should question the weight of such mechanism when compared to the isolating ASA envelope.
The presented approach, making use of quantitative electron density and elemental distribution tomograms to provide nanoscopic 3D colocalization information, is easily extendable to secondary heterogeneous catalysts. While future method developments will aim to increase data acquisition rates, leading to larger field of view and statistical sampling of sample populations, future scientific applications such as elemental migration studies, active-site localization and speciation are envisioned in the field of heterogeneous catalysis.\textsuperscript{5, 7, 31}
Methods:

Materials\textsuperscript{10, 19}

Pristine and deactivated FCC catalyst samples were provided by \textit{W. R. Grace}. Catalysts were manufactured under identical conditions and are based on the same starting formulation. The samples consist mainly of cation-exchanged USY type zeolite, 8\% lanthanum oxide, and kaolin clay. Catalysts are formulated by combining and mixing of aqueous slurries of the individual components, followed by spray drying for initial particle synthesis and a final firing step to increase particle stability.

The deactivated FCC particles were extracted from an industrial FCC unit operating at an increased level of catalyst deactivation, i.e. processing a feedstock which contains on average iron at a concentration of 33 ppm. The catalyst replacement rate in the respective unit was \textasciitilde 0.003 ton of catalyst/ton of processed feedstock. Extracted particles were calcined to remove any residual coke deposits. Secondary additive particles present in the reactor were separated from the FCC particles using a sink/float method. Chemical composition and selected physical properties of pristine and extracted FCC particles are provided in Supporting Table 1.

Electron Microscopy

Industrial FCC units, considering their continuous operation, hold a heterogeneous population of FCC particles with regards to deactivation degree and concurrently impurity loading at any given point in time.\textsuperscript{9} It was henceforth deemed necessary to preselect samples for R-PXCT examination. This was achieved by mounting randomly selected FCC particles onto custom-made tomography pins and examination using EDXS. Particles with the highest iron to aluminium ratio were
chosen for PXCT measurements. A Zeiss Nvision FIB-SEM operated at 18 keV was used for sample preselection.

For scanning transmission electron microscopy (STEM) and corresponding EDXS investigations FCC particles were embedded in epoxy resin cut into fine slices, mechanically thinned and finally ion-milled. High-angle annular dark field-STEM micrographs and EDXS maps were acquired using an FEI Talos microscope operated at 200 kV.

**FCC Catalyst Composition**

Chemical composition of FCC catalysts was determined using an inductively coupled plasma (ICP) technique.

**Powder-XRD**

PXRD measurements were performed using a Bruker D8 Advanced diffractometer equipped with a CuKα1 X-ray source.

**Surface Area Determination**

The surface area of FCC particles was determined by nitrogen physisorption, using a Micromeritics TriStar 3000. Prior to each measurement, the sample was degassed at 300°C for 10 hours.

**Mercury Intrusion Porosimetry**

Mercury PSD measurements were carried out using a Micromeritics Autopore IV 9520 unit. The sample was pre-treated at 200 °C for 15 min, then at 540 °C for 1 h. The pore diameter was calculated using the Washburn equation with a contact angle of 140°.
Resonant Fe-K Edge Ptychographic X-ray Computed Tomography

Ptychographic tomography experiments and data analysis is in part based on earlier publications of ours. An extended description of data acquisition, tomogram reconstruction and analysis can be found in the Supporting Information.

In brief, resonant ptychographic X-ray computed tomography experiments were carried out at the cSAXS beamline of the Swiss Light Source, Paul Scherrer Institut (PSI). The photon energy was either set to 7.123 keV for on Fe K-edge resonance measurements or to 7.310 keV, for off-resonance measurements. A Fresnel zone plate, 150 μm in diameter with an outermost zone width of 60 nm was used to define the illumination onto the sample. The sample was placed ~1.2 mm downstream of the zone plate’s focal point, resulting in an illumination probe of ~3.5 μm in diameter at the sample plane. Coherent diffraction patterns were acquired using a PILATUS 2M detector of 172 μm pixel size, ~7.34 m downstream of the sample. Measurements were carried out using the positioning instrumentation described in Holler et al. with sampling positions set using a Fermat spiral scanning grid with an average step size of 1.2 μm.

Tomography projections were acquired between 0 to 180 degrees using a golden ratio angular acquisition scheme. Around 1100 projections were acquired for each the on and off resonance tomogram. Each projection was obtained by a ptychographic scan of 166 diffraction patterns, each with an exposure time of 0.1 seconds. The field of view covered in each projection was of 40 × 6 μm² (horizontal × vertical). From each diffraction pattern, a region of 400 × 400 pixels was used for the reconstructions. The resulting voxel size in the reconstructed projections is (18.71 nm)² for on-resonance and (18.23 nm)² for the off-resonance measurements.
Reconstructions were obtained with 600 iterations of the difference map algorithm\textsuperscript{51} followed by 600 iterations of maximum likelihood.\textsuperscript{52, 53} After alignment of projections,\textsuperscript{54, 55} tomographic reconstruction of the complex-valued index of refraction was performed using a modified filtered back-projection algorithm (FBP).\textsuperscript{56} The half-period spatial resolution estimate of 39 nm was determined using Fourier shell correlation (FSC), Supporting Figure 1.\textsuperscript{57}

The X-ray dose imparted to the specimen per tomogram was on the order of $2 \times 10^8$ Gy, estimated based on the area flux density during each ptychographic scan and the mass density of the specimen, as described in Howells et al.\textsuperscript{65}

On and off Fe $K$-edge phase tomograms were first resized to the largest voxel size. The 3D data sets were registered using a subpixel image registration approach and resampled onto a common grid. After wavelength normalization the difference between the refractive index decrement tomograms was calculated to obtain the relative iron distribution.\textsuperscript{4, 27} To reduce the experimental noise, we resampled the tomogram to a voxel size of 31 nm. The off-resonance tomogram was converted to electron density to allow the segmentation of catalyst components and to allow the cross-correlation between catalyst component and iron localizations. The absolute, voxel averaged, iron distribution was calculated on the basis of a previously acquired Fe $K$-edge X-ray absorption near edge spectroscopy (XANES) data collected from a hematite reference.\textsuperscript{4, 10} Due to heterogeneities in edge energy ($\pm$2 eV for >95% of iron impurities) the presented iron concentrations possess an inherent uncertainty of ~3% for these impurities, Supporting Figure 2. Combining present uncertainties, \textit{i.e.} uncertainty in electron density determination,\textsuperscript{19} spatial registration, resampling of
tomograms and edge energy, lead to a projected error in iron concentration of around \(~15\%\) on the single voxel level.\textsuperscript{4}
Providing in the Supporting Information is: (1) a detailed Resonant-PXCT experiment and analysis description, including resolution estimate line plots and scattering factor determination, (2) collaborating electron micrographs, (3) pore network analysis plots, (4) table of reference compound values and (5) Supporting Movies.

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Contributions:

I.J., D.A., H.M. and G.-S.M. performed the ptychographic X-ray computed tomography experiments. C.W.-C. and S.Y.Y. conducted bulk characterization experiments and provided samples. I.J., K.F. and M.E. performed EM experiments. I.J., W.K and O.M. analyzed the data. I.J. wrote the manuscript. V.B.J.A. and M.A. led the project, gave conceptual advice, and edited the manuscript. All authors read and approved the manuscript.
**Competing Financial Interests:**

The authors declare no competing financial interests.

**Data Availability:**

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