Localization and Speciation of Iron Impurities within a Fluid Catalytic Cracking Catalyst

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Abstract:

Fluid catalytic cracking refers to a chemical conversion process of industrial scale. This process, utilizing porous catalysts composed of clay and zeolite, converts heavy crude oil fractions into transportation fuel and petrochemical feedstocks. Among other factors iron-rich reactor and feedstream impurities cause these catalyst particles to permanently deactivate. Here, we report on tomographic X-ray absorption spectroscopy measurements that reveal the presence of dissimilar iron impurities of specific localization within a single deactivated particle. Whereas, the iron natural to clay within the composite seems to be unaffected by unit operation, exterior-facing and feedstream introduced iron was found present in two forms. Those being minute quantities of ferrous oxide, located near regions of increased porosity, and impurities rich in Fe^{3+} , preferentially located in the outer dense part of the particle and suggested to contribute to the formation of an isolating amorphous silica alumina envelope.

Fluid catalytic cracking (FCC) is the chemical conversion process used in petroleum refineries worldwide to generate transportation fuel and petrochemical feedstocks from crude oil fractions.^[1] To this end, composites of hierarchical porosity are brought into contact with selected feedstreams at temperatures of around 500°C.^[2] Pristine composite particles are predominantly composed of microporous lanthanum-exchanged NaY zeolites, a crystalline, aluminosilicate and a functional matrix of calcined kaolinite and an amorphous aluminosilicate containing impurities such as iron.^[3] A pristine particle inherently contains around 0.5 wt.% on the basis of iron oxide (Supporting Table 1). Cracking of the feed molecules occurs mainly at the zeolite's active sites located within the composite and connected to the exterior via a network of macro- and mesopores.

Industrial FCC units operate continuously for years on end, repeatedly regenerating composites through calcination at temperatures of up to 800°C. Despite this effort, the catalytic activity of the employed composites decreases over time^[4] necessitating their continuous fractional replacement. The observed decrease is commonly attributed to hydrothermal deactivation and the accumulation of feedstream impurities within the composites.^[1, 5] Due to the continuous nature of operation, oscillating between cracking of feed molecules and catalyst regeneration, impurities within the feedstream, such as nickel, vanadium and iron, can even at ppm levels cause composites to irreversibly deactivate over time.^[4b, 6] For example deactivated particles typically show enhanced levels of iron impurities often up to 2 wt.% of iron oxide.

Studies focusing on feedstream and reactor introduced iron impurities revealed that the formation of iron-rich deposits on a composite's exterior can have potentially dramatic effects on its catalytic performance. These studies suggested catalyst deactivation to occur in addition to zeolite amorphization, by means of pore blocking through physical obstruction^[6b, 6e, 6f, 7] and/ or a coarsening of the particle exterior due to the formation of low-temperature eutectics. The latter results in a dense, apparently non-permeable envelope of amorphous silica alumina (ASA)^[4b, 8] that reduces the catalytic efficiency of a composite particle through a reduction in flux.^[6g, 9] What remains unclear is the nature and role the various iron impurities play in the overall deactivation process.

Here we start to address this topic by visualizing the spatial distribution and speciation of individual iron deposits within an industrially deactivated FCC particle. A hyperspectral tomographic energy dispersive X-ray absorption spectroscopy (tomoXAS) technique applied at the Fe K-edge allowed the retrieval of local X-ray absorption near-edge spectra (XANES)^[10] providing with micron resolution information on local density variation, relative iron concentration, structure, and oxidation state. In conjunction with electron microscopy we here visualize the existence of two impurity subpopulations in a deactivated FCC particle which we suggest to play distinct roles in the overall deactivation process.

Figure 1 presents a schematic of the experimental setup, an example of the Fe K-edge XANES recorded within each voxel (2 μm) and axial plane views (i-iii) of a reconstructed tomographic slice central to the particle. Each view highlights a selected feature of the absorption spectra. (i) X-ray absorption below the Fe K-edge, provides information on sample composition and/ or porosity. The particle is composed to more than 97 wt.% of alumina and silica and contains on average ~20 vol.% of macro- and mesopores.^[8] While the magnitude of detected edge jumps (ii) provides information on the relative iron concentration, the edge energy (iii) provides the oxidation state and speciation of the local iron species. Technical details including the determination of edge jump magnitude and edge energy are provided in the Supporting Methods.

The FCC particle imaged using tomoXAS was extracted from an FCC unit operating at a severe catalyst deactivation. According to advanced cracking evaluation testing the average extracted particle shows a conversion activity loss of ~36% compared to a pristine particle, Supporting Table 1. The investigated particle, ~218 μm by 137 μm , possesses multiple macropores greater than 5 μm . Whereas these macropores are found homogeneously distributed throughout the particle, the overall sample composition is not. Apparent is the existence of a tightly packed outer shell.^[8] This observation is congruent with the relative iron distribution, revealing a more homogeneous distribution within the particle and the accumulation of iron in the particle's most outer layer. This outer layer contains roughly twice the amount of iron as the core. These observations are in line with the recent detection of an iron-enriched dense ASA envelope around deactivated catalyst particles, Supporting Figure 1.^[8] The speciation of iron impurities as given by the absorption edge energy (E_0) follows this trend. The majority of the natural iron in kaolinite within the particle possesses an average E_0 between 7119 and 7123 eV^[3] whereas newly introduced iron or iron close to the particle exterior is either found present as part of the ASA envelope, $E_0 > 7123$ eV, or as a stranded island, $E_0 < 7119$ eV. General verification of these tomoXAS measurements was obtained by XANES and X-ray fluorescence (XRF) measurements of a physical cross section, Supporting Figure 2.

By comparing the observed Fe K-edge energies with those of compounds of known oxidation state, Figure 2a, we can segment the edge energy map according to the average oxidation state within a voxel; i.e. Fe^{2+} , mixed state and Fe^{3+} . Such segmentation allows us in the first instance to visualize spatial tendencies in oxidation state, Figure 2b, and, secondly, by summation of the isolated voxel it permits the retrieval of XANES of sufficient quality, to visualize the pre-edge absorption peak, Figure 2c&d. Mixed state voxel can be a result of a mixture of catalyst components either dominant in Fe^{2+} or Fe^{3+} on the single voxel level or a single catalyst component of roughly equal composition. Only areas in which edge jump magnitude extraction and XANES normalization were achievable were considered for analysis, Supporting Methods.

Looking at the edge energy histogram and the corresponding oxidation state map, Figure 2a&b, around 30% of the voxels are dominated by iron impurities in the form of Fe^{3+} , <1% in the form of Fe^{2+} , and 69% of an $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixed valence state with different Fe^{2+} and Fe^{3+} proportions.^[11] Further, we can see that the outer ASA envelope occludes mostly Fe^{3+} or iron species with an edge energy greater than 7123 eV. Within the interior of the particle, we observe a continuous mixture of Fe^{3+} and Fe^{2+} interspersed with what appears to be

hotspots of Fe^{3+} dominated voxels. Regions dominant in Fe^{2+} are found as stranded islands that are spatially closely associated with regions of decreased absorption.^[12]

Focusing on the pre-edge absorption peak intensity and shape of these groups, Figure 2d, we can further query the geometry of the iron atom. This is due to the fact that the pre-edge absorption peak arises from the formally forbidden $\text{Fe } 1s \rightarrow 3d$ transitions which become allowed in reduced symmetry environments and as such are sensitive of the oxidation state and geometry of the iron atom.^[12-13] From the positive correlation of oxidation state increase and increasing peak intensity we can defer a transition from predominantly centrosymmetric six-fold coordinated iron to a mixture increasing slightly in non-centrosymmetric four-fold coordinated iron with increasing edge energy.^[3] Further the absence of any defined pre-edge features such as energy splitting in contrast to measured reference compounds, Supporting Figure 3, suggests that defined groups contain iron species of more than one oxidation state i.e. a result of summation to visualize the pre-edge and/ or a mixture of iron impurities on the single voxel level.^[13b]

Linear-combination fitting of one these groups further revealed that the average Fe^{2+} dominated voxel is best described by a combination of ferrous oxide (FeO) ~48 wt.%, metallic iron (Fe) ~27 wt. %, and ferrosilite (FeSiO_3) ~23 wt.%, among the measured reference compounds, Supporting Figure 3 and 4.

The preferential localization of Fe^{2+} in low density regions and the above implied presence of FeO particulates,^[6e, 6f, 7] can find further support in a more quantitative perspective. Such a perspective can be obtained when we consider how iron-rich the segmented voxel are, Supporting Table 2. Voxel dominated in Fe^{2+} contain about 20% less iron than the ensemble average voxel. These voxels are however also the ones that show the lowest packing density. Normalization with regards to the measured absorption below the Fe K-edge, Figure 1 (i), decreases this difference to ~8%. This suggests further that occluded iron in these voxels is present in particulate form rather than part of the matrix. The reverse is observed for Fe^{3+} dominated voxel.

A graphical representation of this co-localization and, in extension, the correlation between packing density (i), relative iron concentration (ii) and oxidation state (iii) is presented in Figure 3. This representation was obtained by merging the absorption and edge jump maps shown in Figure 1a&b. The degree of colocalization was further determined using intensity cross correlation-based analysis.^[14] A calculated Pearson coefficient, r , of 0.83 is indicative of partial co-localization whenever both signals are significant but that individual regions exist, i.e. regions of increased density but low iron concentration and vice versa. This observation is well reflected in the graphical representation showing a strong correlation in the outer circumference of the particle while less correlated regions are found in the particle interior.

A merger of density, iron concentration and oxidation state maps, Figure 3c, further stresses that segregation of iron impurities depending on their respective oxidation state is found present. Fe^{3+} is preferentially found in regions of increased density and iron concentration. Fe^{2+} in low density, low iron concentration regions. This segregation however only holds true for the outer regions of the particle. The core of the particle, showing lower levels of iron and an overall more heterogeneous oxidation state distribution, appears to be unaffected by introduced impurities.

The spatial extent of such co-localization, the iron speciation itself, and in turn, the suggested deactivation process, e.g. flux and active site reduction by means of ASA envelope formation, can find their origin in part in the unit operation profile. The exposure of FCC particles to such contrasting environments in rapid succession (reaction-regeneration cycle) can lead to a situation in which intrusion depth and speciation profile of impurities are determined by kinetic factors. The intrusion depth and speciation of impurities are thusly defined by unit operation conditions, in particular regenerator temperature and residence time, number of operation cycles experienced and feed contaminant level.^[6e, 8] Following the hypothesis of Yaluris et al.^[4b], suggesting an iron-induced formation of low-temperature eutectics, such limitations could over time give rise to the formation and growth of the iron-rich ASA envelope, whose spatial extent in turn is predetermined by the intrusion depth of feedstream-introduced iron impurities.^[6e, 6g, 7-8]

The iron speciation, most dominant in Fe^{3+} in this outer envelope can be explained by the interaction tendencies of iron with zeolite^[15] and kaolin^[3]. Iron impurities natural to kaolin are generally found present in the form of six-fold coordinated Fe^{2+} or Fe^{3+} either substituting for Al^{3+} in the kaolin structure itself or as an amorphous coating with minor occurrences of ferrous oxide.^[3] With increasing temperature and the congruent transformation to metakaolin at $\sim 500^\circ\text{C}$ and its progressive amorphization to an eventual mullite precursor at $\sim 900^\circ\text{C}$ ^[8, 16] these iron impurities increasingly substitute Al^{3+} in the distorted tetrahedral environment of the metakaolin. The iron impurities in question thereby shift from a six-fold coordination to four-fold coordinated Fe^{3+} as reflected in the pre-edge absorption increase, Figure 2. Similar observations have been made for zeolites.^[6g, 15] Substitution of Al^{3+} with Fe^{3+} in the faujasite lattice leads to a reduced thermal stability of the zeolite, with reported onset temperatures of amorphization below 700°C .^[15] Detected ferrous oxide impurities could either originate from the feedstream or from the reactor.

Considering the operational temperature range and measured impurity speciation we can postulate that feedstream-introduced iron impurities catalyze the amorphization of zeolites close to the particle exterior.^[8] In combination with suggested low-temperature eutectics^[4b] and local hotspots and upon recombination with the already amorphous metakaolin, such amorphization could lead to the formation of the apparently non-permeable ASA envelope. Both factors could contribute the deactivation of the catalyst particle by reducing the overall number of active sites and the ease of access of the remaining active sites. The detection of impurities best described by ferrous oxides or metallic iron in regions of low sample density, given the low spatial resolution cannot be taken as a direct confirmation of any deactivation mechanism. This includes the deactivation through physical obstruction of selected pores.^[6e, 6f, 7-8, 9b] A mechanistic understanding of impurity uptake and incorporation remains similar elusive.

In summary, the application of a recently developed hyperspectral tomographic imaging technique allowed the identification of dissimilar iron impurities of specific localization within a deactivated FCC particle. The results presented suggest the possibility of impurity driven, selective deactivation mechanisms.

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Figure 1: Scanning Tomographic X-Ray Absorption Spectroscopy of an FCC Particle. Shown in the top panel is a schematic of the experimental setup. Using a polychromatic fan and a position sensitive detector, a set of tomographic projections (ϕ) were collected. Each consisting of a line scan, step size 2 μm , central to the particle ($\square\square\square$). Shown electron micrograph (--) is representative of a typical FCC particle. Analysis of the acquired projections as a function of position and rotation allowed the construction of one sinogram per energy which can be used to reconstruct a spectro-tomographic volume in which each voxel ($\square$) contains a full Fe-K edge XANES (7080-7180 eV). Provided in the bottom panel are orthoslices slices central to the particle each highlighting selected features in the XAS data, namely (i) absorption below the edge, indicative of density of the material, (ii) edge jump magnitude normalized with respect to the presented field of view, showing the local iron concentration, and (iii) Fe K edge energy, revealing the iron speciation. ii and iii: selected voxels were rejected from analysis due to insufficient iron concentration or failing XANES normalization), Supporting Figure 5.

Figure 2: Oxidation State Assignment, Segmentation and XANES. a) Shown is the Fe K-edge energy histogram of the imaged FCC particle alongside the edge energy of reference compounds of known oxidation state ranging from Fe²⁺ to Fe³⁺. b) Based on the highest / lowest edge energy of the reference compounds with regards to a single oxidation state we segmented the measured edge energy map into 3 groups, voxels dominant in "Fe²⁺", "Fe³⁺" or presenting a mixed state ("Fe²⁺/Fe³⁺"). Mixed state voxel can be a result of a mixture of catalyst components either dominant in Fe²⁺ or Fe³⁺ or a single catalyst component of roughly equal composition. Scale bars are 50 μm. c) Fe K-edge XANES of the individual groups obtained by summation and subsequent normalization of the segments. Further given is the XANES of the entire particle. d) Line plots highlighting changes in the pre-edge absorption after subtraction of the edge feature.

Figure 3: Colocalization of Iron Impurities Occluded within a Deactivated FCC particle with Regards to Iron Concentration and Sample Density. Shown in a) are tomographic slices central to a catalyst particle highlighting the relative variations in sample density (ΔSD), iron concentration ($[Fe]$) and oxidation state/ number (ON) and their representation in a monochromatic colour map. Provided in b) are colour merged images of these monochromatic orthoslices alongside expanded versions of selected areas providing a visual representation of the colocalization of variations in sample density and iron concentration, density and oxidation state, and iron concentration and oxidation state. c) Merged imaged of all 3 variables. Stressed is the increased degree of colocalization at the edge of the particle throughout the presented images. The scale bars in b) are common to all maps.

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Conflict of interest:

The authors declare no conflict of interest.

Data Availability:

Data that support the findings presented are available upon request from the corresponding authors.

Table of Contents Entry

Tomographic X-ray absorption spectroscopy at the Fe-K edge allowed the visualization of distinct iron impurities of specific localization within a single deactivated fluid catalytic cracking catalyst particle. Spatial localization in combination with iron impurity speciation is in agreement with a multimodal deactivation process.