Supporting Information

Visualizing Dealumination of a Single Zeolite Domain in a Real-Life Catalytic Cracking Particle

Sam Kalirai, Pasi P. Paalanen, Jian Wang, Florian Meirer, and Bert M. Weckhuysen*

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S1. Thin Sectioning

Two spent FCC catalyst particles (labeled as ECAT1 and ECAT2) were obtained from an FCC unit, while the fresh FCC catalyst under study has been provided by Albemarle. Details of the fresh FCC catalyst material have been reported in previous research work. Approximately 0.5 mg of FCC catalyst sample from the fresh and aged FCC catalyst materials were embedded in an epoxy resin and microtomed to 500 nm thin sections using an Ultracut E Reichert-Jung microtome (Leica) equipped with a glass knife. The sections were placed on a 50 mesh copper EM grid coated with Formvar.

S2. Scanning Transmission X-ray Microscopy

Micro-spectroscopic measurements were performed on the microtomed sections of the fresh and two aged FCC catalyst particles using the Scanning Transmission X-ray Microscope (STXM) at SM beamline 10ID-1 of the Canadian Light Source (CLS). The X-ray absorption at the Al K-edge, La M$_{5,4}$-edge, and Fe L$_{3}$-edge were measured for thin sections of the individual FCC catalyst particles, providing insight in the zeolite aggregate domains (i.e., Al and La), the metal poisons (i.e., Fe) and matrix material (e.g. Al). In total, one FCC catalyst particle from the fresh sample and two aged FCC catalyst particles (ECAT1 and ECAT2) were measured. Due to the low concentration of Ni, it was not possible to measure Ni for the aged FCC catalyst particles. At each measured edge, a fixed scan step (i.e. pixel) size of 100 x 100 nm was used to scan a field of view encompassing the whole FCC catalyst particle sections, which were approximately 40-50 μm in diameter. The Al K-edge XANES data stacks for each FCC catalyst particle were energy calibrated by concurrently measuring ZSM-5 as a reference standard sample with known white line centered at 1566.0 eV. Analysis of the STXM data was performed using the aXis2000 software package to yield optical density (OD) stacks at each edge. The matrix deconvolution procedure, non-negative linear combination fitting of the Al K-edge data stacks/spectra and zeolite domain segmentation was performed using an in-house developed MATLAB code. Zeolite Y and ZSM-5 were measured at the CLS 10ID-1 STXM beamline, whereas the reference spectra for kaolin, boehmite, α-alumina and γ-alumina originate from earlier measurement campaigns (see References 2 and 3).[2,3] The zeolite H-Y reference sample was provided by Albemarle (Si/Al = 5.5), while the NH$_{4}^{+}$-ZSM-5 sample was obtained from Zeolyst (ID: CBV 2314, Si/Al = 11.5, Surface Area = 425 m$^{2}$/g). The reference spectra of ZSM-5, γ-alumina, kaolin and boehmite were used in the linear combination fitting of the matrix components of the FCC catalyst particle (section S5). Zeolite Y was used for comparison against the deconvoluted zeolite spectra.

S3. X-ray Fluorescence Microscopy

X-ray fluorescence microscopy was performed on the same ECAT1 and ECAT2 particle thin section samples that are presented in the paper, in order to determine the elements that are present and their relative concentrations. The XRF measurements were performed at the European Synchrotron Radiation Facility, beamline ID21. The measurements were performed with a 500 x 500 nm x-ray spot size at 8.5 keV in order
to obtain information of all relevant elements. Fig. S1 shows the resulting elemental maps after performing a fit on the XRF spectra using PyMCA analysis software. La denotes the zeolite domains present in the sample, and are consistent with those measured using STXM. In order to confirm our catalytic age determination, the relative amount of each element was determined for the ECAT1 and ECAT2 particles. It can be seen from Fig. S2 that ECAT2, in comparison to ECAT1, has higher relative amounts of the deposited elements (i.e., Fe, Ni, and Ca) suggesting again that it is catalytically “older”. Furthermore, the metals Fe, Ni and Ca are seen to form a ring around the outer edges of the particle, presumably deposited via feedstock molecules containing metals. V, which also acts as a poison, is seen to be present in the interior of the FCC catalyst particle. Whereas Fe, Ni and Ca can deactivate the catalyst by changing its accessibility, V is known to promote destruction of the zeolite via formation of vanadic acid.[4,5] However, the majority of the studies on zeolite destruction caused by V have been focusing on isolated zeolites or synthetic laboratory conditions with artificially high levels of V. Here, by looking at the V distribution on the FCC catalyst particle, it can be seen that the high intensity La areas have correspondingly lower V present. This is exemplified in the ECAT2 sample where the large zeolite region at the bottom has a corresponding low intensity of V. In order to quantify whether there were any spatial correlations between the relevant elements, the Pearson correlation coefficients of each element pair were determined for the ECAT1 (Table S1) and ECAT2 (Table S2) catalyst particles. It can be seen that V has a high correlation to Al and Si, but the corresponding correlation to La is much lower, suggesting that the V is largely present in the matrix component of the FCC particle and not in the zeolites. This suggests that the matrix plays a significant role in passivating V before it enters into the zeolite domains.[6] The other poison metals, namely Fe, Ni and Ca, have high correlations with one another, suggesting that they are co-deposited and have similar deposition mechanisms. This has been previously observed in XRF measurements by our group.[7]
Figure S1. Elemental XRF maps for the ECAT1 and ECAT2 catalyst particle thin section samples. Elements inherent to the FCC particle (Al, Si, La and Ti) as well as acquired/deposited elements (Fe, Ni, Ca and V) in/on the FCC particle can be simultaneously measured.
Figure S2. Average XRF counts of the poison metals Fe (red), Ni (green) and Ca (blue) for the ECAT1 and ECAT2 catalyst particle compared to the average % tetrahedral Al present in the zeolite domains of the fresh, ECAT1 and ECAT2 catalyst particles.

Table S1. Pearson correlation coefficients of each elemental pair as determined by the XRF maps for the ECAT1 catalyst particle.

| Element | Al   | Si   | Ti   | La   | Fe   | Ni   | V   |
|---------|------|------|------|------|------|------|-----|
| Al      | 1.000|      |      |      |      |      |     |
| Si      | 0.849| 1.000|      |      |      |      |     |
| Ti      | 0.344| 0.307| 1.000|      |      |      |     |
| La      | 0.628| 0.797| 0.198| 1.000|      |      |     |
| Fe      | 0.372| 0.404| 0.188| 0.265| 1.000|      |     |
| Ni      | 0.328| 0.350| 0.159| 0.244| 0.866| 1.000|     |
| V       | 0.820| 0.700| 0.306| 0.464| 0.436| 0.416| 1.000|
| Ca      | 0.324| 0.383| 0.149| 0.299| 0.796| 0.731| 0.367|
Table S2. Pearson correlation coefficients of each elemental pair as determined by the XRF maps for the ECAT2 catalyst particle.

| Element | Al  | Si   | Ti   | La  | Fe  | Ni  | V    |
|---------|-----|------|------|-----|-----|-----|------|
| Al      | 1.000 |     |      |     |     |     |      |
| Si      | 0.752 | 1.000 |      |     |     |     |      |
| Ti      | 0.321 | 0.304 | 1.000 |     |     |     |      |
| La      | 0.471 | 0.659 | 0.067 | 1.000 |     |     |      |
| Fe      | 0.400 | 0.372 | 0.179 | 0.156 | 1.000 |     |      |
| Ni      | 0.534 | 0.448 | 0.188 | 0.225 | 0.896 | 1.000 |      |
| V       | 0.854 | 0.620 | 0.257 | 0.354 | 0.397 | 0.533 | 1.000 |
| Ca      | 0.257 | 0.247 | 0.103 | 0.146 | 0.611 | 0.587 | 0.255 |

S4. Matrix Deconvolution Method

It is known that FCC catalyst particles are a mix of different Al and Si rich phases that are present in the matrix. The zeolites, which are low-density, highly porous crystalline aluminosilicate materials, are embedded within the FCC catalyst particle matrix, making the spatial and chemical segmentation of zeolite domains very challenging. Since the zeolite materials that are typically used in FCC catalysis are of the zeolite Y type, they contain most often La. As a consequence, La can be used as a marker to identify and segment the individual zeolite aggregate domains within the individual FCC catalyst particle. In order to extract the Al K-edge XANES of each zeolite aggregate domain, we have performed a deconvolution procedure to remove the component signal of the FCC catalyst matrix. Since the STXM measurements are performed in transmission mode, the incoming X-rays probe the total thickness (i.e., 500 nm) of the FCC catalyst particle. The resulting X-ray absorption signal is thus a convolution of the probed FCC matrix materials and the probed zeolite Y material through the sliced FCC catalyst particle at a specific point. This reasoning is illustrated in Fig. S3. The signal from the FCC catalyst matrix is appreciable even when the zeolite Y component represents the majority of the probed thickness since the density, and thus the X-ray absorption coefficient of the zeolite material, is much lower than that of the matrix material.[8]
Figure S3. The X-rays are transmitted through the FCC catalyst particle slice for detection. The La map can be used to determine the position of the aggregate domains of zeolite Y, however due to the non-zero thickness of the FCC catalyst particle sample, the detected signal is a convolution of the embedded zeolite and matrix materials.

Provided there is a constant zeolite density and uniform La concentration throughout the zeolite aggregate domains in a FCC catalyst particle, the intensity of the La map (i.e. mass absorption coefficient) will be linearly related to the thickness of the zeolite domain. Furthermore, since the electronic transition of the M_5 edge is into the tightly bound, empty density-of-states of the 4f orbitals, the transition is highly insensitive to any chemical changes the La may experience as a function of catalyst age thus making it an excellent marker over the fresh and aged FCC catalyst particles. In order to illustrate this, the La spatial map was segmented based upon their La intensity. The masks created by each La intensity interval ranging from 0.4-2.0 ΔOD (i.e. the difference in optical density “on peak” from pre-edge; ΔOD = OD_{peak} – OD_{pre-edge}) were then used to extract the Al K-edge signal for each respective interval for each sample. Fig. S4 plots the Al K-edge XANES of each La interval mask for the fresh FCC catalyst particle sample. It can be seen that as the average intensity of the La increases, a peak at 1566.5 eV increases (black vertical line), signifying a larger contribution from the zeolite domain. This clearly shows that the resulting spectrum is a convolution of the matrix and the zeolite components.

In order to obtain the raw zeolite signal, the pure signals derived from the matrix and the zeolite used to perform a non-negative linear combination fit of the Al K-edge XANES of the resultant La interval masks. The signal for the matrix was obtained by masking the La map at ΔOD below 0.04, whereas the signal for the zeolite aggregate domains was obtained by masking the La map at ΔOD above 2.2. By obtaining the reference spectrum of the matrix from the sample itself ensures that any intra-particle variances in the density and chemical nature of individual FCC catalyst particles are best accounted for. These differences are apparent in comparing the matrix signal of the fresh and aged catalyst particles. This is due to the apparent shift of the matrix chemistry from a Boehmite/Kaolin mixture to γ-alumina. The result of the fitting for the fresh FCC catalyst particle sample is shown in Fig. S5. It can be seen that the fitting results show a strong linear relationship between the amount of matrix fitting and the La ΔOD intensity.
Figure S4. Al K-edge spectra of the fresh FCC catalyst particle as masked at different La threshold ranges from 0.4-2.0 ΔOD. The stacked spectra show a growth in a shoulder/peak at 1566.5 eV corresponding to the signal from the zeolite fraction.

Figure S5. Fit results of the fraction of the matrix spectrum (red) and the zeolite spectrum (blue) fitted to the Al K-edge XANES at different average La intensities for the fresh FCC catalyst particle. The trend shows a strong linear relationship between the average La intensity and the fitted matrix.

Since the fitting of the matrix of the FCC catalyst particle was performed on the averaged spectrum, the linear correlation of the matrix component to the average La intensity is high. However, in order to fully remove the matrix component from the signal, the fit was performed on a zeolite-by-zeolite basis to account for local density variations in the matrix. In this procedure, we have only considered zeolite domains that were larger than 25 pixels in order to ensure sufficient statistics of the signal. Fig. S6 plots the mean La ΔOD intensity against the percentage zeolite component that was fitted to the zeolite for the fresh FCC catalyst particle. As can be seen, there remains a strong linear correlation of the fitting with respect to the mean La intensity of the domain in the fresh FCC catalyst particle.
Figure S6. Scatter plot showing the mean La ΔOD intensity plotted against the percentage of the total fit that was zeolite for individual zeolite domains (blue dots) of the fresh FCC catalyst particle.

Fig. S7 plots the result of the average Al K-edge XANES of all the zeolite aggregate domains after subtraction of the matrix signal. Also plotted is a zeolite Y reference spectrum, and it can be seen that the resulting spectrum closely matches the zeolite Y reference signal (despite not being used in the deconvolution). Thus, the fitting results clearly show that the matrix deconvolution method is valid and that the contribution of the matrix to the resulting XANES may be confidently determined, and subsequently be removed.

Figure S7. The resulting spectrum of the zeolite domains of the fresh FCC catalyst particle (blue; as masked by the La map) after subtraction of the matrix. The spectrum shows a close resemblance to that of the zeolite Y reference spectrum (orange).
The same deconvolution procedure was performed on the two aged FCC catalyst particles. The scatter plot plotting the mean La intensity versus the percentage zeolite fit for each individual zeolite aggregate in ECAT1 (top, green) and ECAT2 (bottom, red) domain is shown in Fig. S8. The resulting zeolite domain Al K-edge spectra of the ECAT1 and ECAT2 particles are shown in Fig. S9. It can be seen that the spectra show characteristic differences to the reference zeolite Y spectrum, thus signifying that differences in the spectral features are captured using the developed method.

Figure S8. Scatter plot showing the mean La ΔOD intensity plotted against the percentage of the total fit that was zeolite for individual zeolite aggregate domains (red dots) for the ECAT1 (top, green) and ECAT2 (bottom, red) catalyst particles.
Figure S9. Resulting Al K-edge XANES of the ECAT1 (green) and ECAT2 (red) catalyst particle and a zeolite Y reference sample (Orange) after removal of the matrix.

S5. Least squares fitting of the Deconvoluted Zeolite Spectra

The deconvoluted spectra of the average and single zeolite domains of the catalyst particle samples were then used to determine the relative tetrahedral and octahedral Al present. A non-negative linear combination fitting was performed with three reference spectra, representing possible coordination environments of Al. A fresh zeolite ZSM-5 sample was used as a 4-coordinated aluminum reference, as it is known to contain exclusively 4-coordinated Al\(^{[9]}\), α-alumina was used as a pure 6-coordinated aluminum-oxide species\(^{[10]}\) and boehmite was used as a 6-coordinated aluminum-oxyhydroxide species.\(^{[11]}\) The Al K-edge XANES of the reference spectra can be seen in Fig. S10. The spectrum for ZSM-5 was measured concurrently with the measurement of the three FCC catalyst samples as it was also used to provide an energy calibration for the resulting data stacks. The spectra of α-alumina and boehmite were already obtained in previous measurement campaigns.\(^{[2,3]}\)
Figure S10. Al K-edge XANES spectra of reference compounds, boehmite (a), α-alumina (b) and ZSM-5 (c). The spectra were used to perform non-negative linear least squares fitting of the deconvoluted zeolite spectra to determine the tetrahedral (4-coordinated) and octahedral (6-coordinated) Al.

S6. Analysis of the Al K-edge XANES from the Matrix

The Al chemistry of the matrix was also analyzed for all three catalyst particles presented in the paper and is presented in Fig. S11. We have investigated Al K-edge XANES spectra of the matrix component (Fig. S11a), which shows that the XANES from the fresh FCC catalyst particle clearly differs from that of the ECAT particles suggesting that there are differences in the Al chemistry of the matrix as the particle ages. To understand the chemical changes occurring in the matrix, a linear combination fit of the reference spectra of 4-coordinated Al, kaolin, boehmite and γ-alumina was performed on a pixel-by-pixel basis of the Al K-edge data stack and is summarized in Fig. S11b as component maps for each sample. The fresh sample is dominated by a combination of boehmite and kaolin with γ-alumina appearing only as a minor component. In the ECAT particles γ-alumina represents the dominant phase of the matrix. γ-alumina is a catalytically active phase in cracking, and thus is essential for the pre-cracking functionality in the FCC catalyst matrix. The formation of γ-alumina can occur via the calcination of boehmite at 500-600°C, thus given the presence of boehmite in fresh FCC catalyst particles, the physical conditions within the FCC unit will promote the formation of γ-alumina. Furthermore, it can be expected that the longer an individual FCC catalyst particle has experienced reactor conditions, the larger the amount of γ-alumina present in the matrix. The presence of γ-Alumina in ECAT particles has been previously observed in μ-XRD measurements and is confirmed by our STXM measurements. In addition, STXM shows the presence of γ-alumina is related to the presence of boehmite and that the fractional amount of γ-alumina correlates with the catalytic age of ECAT1 (82.52%) and ECAT2 (88.74%). Surprisingly, very little kaolin is
present in the ECAT particles, suggesting that there may also be a transformation of kaolin into another Al phase, such as mullite, as recently determined with X-ray diffraction.\textsuperscript{[13]}

\begin{figure}
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\caption{Figure S11. a) The average Al K-edge XANES extracted from the matrix component of the FCC particle. b) False colored linear combination fit maps of Fresh, ECAT1 and ECAT2 particles with 4-coordinated Al, Kaolin, Boehmite and γ-alumina (plotted on the same scale) shows the shift from a Kaolin and Boehmite dominated matrix in the Fresh sample towards the formation of γ-alumina in the ECAT samples.}
\end{figure}
S7. Determining Relative Age of Measured Particles

The relative catalytic age of the ECAT1 and ECAT2 catalyst particles was determined by quantifying the relative amount of Fe that was deposited on each FCC catalyst sample. In FCC, catalyst particles are exposed to a crude oil-derived feedstock, which contains metals, such as Fe. During catalytic cracking, Fe gets deposited onto the FCC catalyst particle and due to its low mobility Fe predominantly remains on the outer layers of the catalyst particle. By measuring the amount of Fe on the FCC catalyst particles it can be determined how long, or how many successive cycles of the FCC process an individual catalyst particle has experienced, thus giving an indication of the catalytic age of the particle. Since Fe can also be present in lower concentrations inside the clay portion of the catalyst we expected that the fresh catalyst particle also had Fe present in the sample. Thus we have measured the average Fe concentration that is present in the whole FCC catalyst particle for all three samples, i.e., fresh, ECAT1 and ECAT2, using the fresh FCC catalyst particle as an arbitrary baseline. The Al K-edge elemental map of each particle was thresholded to make a binary mask of the whole FCC catalyst particle. The mask was then used on the aligned Fe map to determine the average Fe ΔOD. The results are shown in Fig. S12. It can be seen that the ECAT2 (0.068 ΔOD) shows the highest average Fe concentration, whereas that for the ECAT1 particle is lower (0.041 ΔOD), but still clearly higher than the one for the fresh FCC catalyst particle (0.014 ΔOD). Since the Fe is present on both ECAT1 and ECAT2 at levels higher than the fresh catalyst particle, we conclude that this was due to deposited Fe from catalytic aging.[7,14] Furthermore, due to the higher Fe content in the ECAT2 particle, we anticipate in view of our previous work on FCC catalyst characterization that the ECAT2 catalyst particle is “catalytically older” than the ECAT1 particle.[1,7,15] This result confirms the XRF results (Tables S1 and S2), showing an increased content of all metal poisons for the ECAT1 catalyst particle.

Figure S12. The average intensity of the Fe elemental map was calculated over the whole FCC catalyst sample. The average intensity for the three FCC catalyst particles shows that for the fresh FCC catalyst particle there is very little Fe present (ΔOD 0.01), whereas for the ECAT1 catalyst particle (ΔOD 0.04) and the ECAT2 catalyst particle (ΔOD 0.07) there is an appreciable amount of Fe present. Inspection of the spatial maps of all three particles shows that most of the Fe that is present in the E-Cat samples has been deposited on the exterior of the catalyst particles. Due to the limited mobility of Fe the cumulated intensity was used to classify ECAT2 as “catalytically older” than
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