Supporting information for "A DNP-supported solid-state NMR study of coke species in Fluid Catalytic cracking catalysts, Deni Mance, Johan van der Zwan, Marjolein E.Z. Velthoen, Florian Meirer, Bert M. Weckhuysen, Marc Baldus, Eelco T.C. Vogt

A. SEM-EDX measurements

For performing the SEM-EDX measurements, the FCC particles under study (without pretreatment) were deposited on an aluminum stub and fixed by means of a carbon slab. Subsequently, a thin Au/Pd layer of 15 nm thick was sputtered on the FCC particle in order to prevent charging in the SEM. The SEM image was measured using a secondary electron detector. Secondary electron images are especially suited for showing surface morphology. Tables S1 and S2 provide the experimental details and instrument settings for the SEM and SEM-EDX measurements, respectively.

In order to be able to measure cross sections of the catalyst samples, a number of representative FCC particles were imbedded in resin, grinded/polished and coated with a carbon layer of about 5 nm thick. Figure S1 shows a backscattered electron image on the top and an Fe concentration map, expressed in net counts, of the same area on the bottom. In backscattered electron images, the brightness of each individual pixel is determined by the average atomic number of the sample at that particular position. The higher the average atomic number, the brighter the corresponding pixel will be. Therefore, the difference in contrast gives information about the composition and location of the different constituents. It should be noted that, although the effects of a higher average atomic number by different elements are much stronger, density differences or micro-porosity with pore sizes smaller than the lateral resolution, can have a similar effect.

Pre-treatm	ent / drying	Imbedding			Stub
Temp.	Pressure	time	Resin	Pressure	Mounting
70 °C	200 mbar	1 h	LR-White	100 mbar	Carbon slab

Table S1 SEM specimen preparation conditions

Grinding/Polishing (Struers Tegramin-25)					
Grain		Time (s)	Pressure (N)	Lubricant	Diamond
P500	x	10	20	IPA	-
P800	x	15	20	IPA	-
P1000	x	15	20	IPA	-
P1200	x	20	20	IPA	-
P2400	x	60	20	IPA	-
P4000	x	180	20	IPA	-
DUR	x	300	15	IPA	1µm

EDX analysis for Iron was performed on 19 FCC particles. Approximately half of these particles showed a clear concentration of iron in a surface shell already at visual inspection. Figure S1 is representative for this class of FCC particles. The other half of the particles show less clear

concentration distribution upon visual inspection, but did show a clear radial dependence of the Fe concentration distribution when the radial distribution was calculated. Figure S2 is representative for this class of FCC particles.

The iron distribution images were prepared by reading in the matrix of iron-counts from the SEM-EDX into MATLAB, and preparing a color-coded image, where the color-coding range was determined by the histogram of count values. The color-coding is the same for both images shown here.

	Image	Mapping
Source	LaB ₆	LaB ₆
EHT (kV)	8	20
Spot size (a.u.)	300	600
Beam Current	22 pA	4.2 nA
Aperture (µm)	20	30
Working distance (mm)	11.0	11.0
Mode	Ana	Ana
Detector (s)	SE	EDX
Live time (s)	-	-
Number of frames	-	160
Frame time (s)	-	20
Dwell time (s)	-	50
Rate meter setting	-	Auto
Number of points	1024x768	1024x768

Table S2 SEM and EDX Measurement conditions for the Zeiss EVO MA15-Noran system 7 instrument.



Figure S1: An example of a SEM-EDX image where visual inspection already clearly indicates iron concentration in a surface shell of approximately 3.5 micrometer. The pixel size is 0.181 by 0.181 micrometer, so the total image measures approximately 185 by 139 micrometers. Top: backscattered electron image; Bottom: Fe concentration map expressed in net counts of the same area.



Figure S2: An example of a SEM-EDX image where iron concentration is not immediately clear from visual inspection. The statistical analysis of the image in Figure S4 shows that there is nevertheless a concentration of iron at the surface. The pixel size is 0.155 by 0.155 micrometer, so the total image measures approximately 158 by 119 micrometers.

The SEM-EDX images have been processed to determine the radial concentration distribution of Fe in the cross sections of the imaged FCC catalyst particles. Figures S3 and S4 show the image processing steps performed to obtain the Fe concentration as a function of distance from the particle surface for the same two data sets as shown in Figure S1 and S2. First, the original image was cropped and a region of interest was selected that contained the particle of interest. Next the image was binned using a binning factor of 5 pixels in both x and y direction. The binned image was rescaled to contain values in [0 1] and then thresholded using a value of 0.7 to obtain a binary image. The binary image was further processed by filling regions and holes within the particle using an algorithm based on morphological reconstruction [1]. Next, the binary mask was filtered removing isolated pixels and regions smaller than 100 pixels using a 4-connected neighborhood. The resulting mask was then scaled back to the original resolution of the image using bicubic interpolation. Finally, the distance map was calculated using the Euclidean distance transform of this (binary) mask [2]. Here the Euclidean distance is defined as the straight-line distance between two pixels.



Figure S3: Image processing steps to obtain the distance map used for calculating the Fe concentration as a function of distance from the particle surface of FCC particle 1 (as seen in figure S1). The scale bars in the top three figures indicate the number of raw or binned counts per pixel. In the middle three images and the left two bottom pictures, the scale bars indicate the normalized pixel values. In the bottom right picture, the scale denotes the minimum distance to the edge of the particle in pixels.



Figure S4: Image processing steps to obtain the distance map used for calculating the Fe concentration as a function of distance from the particle surface of FCC particle 2 (as seen in Figure S2). The scale bars in the top three figures indicate the number of raw or binned counts per pixel. In the middle three images and the left two bottom pictures, the scale bars indicate the normalized pixel values. In the bottom right picture, the scale denotes the minimum distance to the edge of the particle in pixels.

This resulted in a data set where each pixel inside the particle cross-section (i.e. pixels with a value of 1 in the final binary mask) was assigned two values: a distance from the surface of the particle using number of pixels as the unit of length and the Fe (relative) concentration, expressed in counts (i.e. as recorded by SEM-EDX). Distances have been rounded to single integer pixel values. Next all pixels with the same distance to the particle surface were pooled and used to calculate the mean Fe counts for each distance. For comparison two mean values were determined: one including pixels with zero counts and one excluding those pixels. Furthermore the standard deviation and the number of pixels at the same distance were calculated.

Figures S5 and S6 show the results of the evaluation, namely the relative Fe concentration as a function of distance from the particle surface.

These data are in excellent agreement with recent previous studies of our group showing an enrichment of Fe in the surface of equilibrium FCC particles [3-9].



Iron concentration as function of distance to surface (in pixels)

Figure S5: Fe concentration as a function of distance from the particle surface of FCC particle 1.





Figure S6: Fe concentration as a function of distance from the particle surface of FCC particle 2.

The Fe-counts reported in this analysis for points at largest distance from the surface (the right sides of the plots) fluctuate more wildly than the counts reported for distances closer to the surface. This is because, for the large distance values, the number of pixels sampled to arrive at the mean is very small, whereas at the same time the data is speckly. The seemingly large values in the center of the particle are thus artificial.

The procedure was then repeated for all 19 particles. The graphs of iron concentration versus distance from particle surface were normalized to the average for the range of 100-200 pixels from the surface. Because not all particle particles have the same diameter, the distance range was limited to 200 pixels from the surface. The resulting graphs are shown in Figure S7. The bottom part of Figure S7 shows a stacked graph constructed from summing the individual graphs, in essence creating a moving average.



Iron concentration as function of distance to surface (in pixels)



Iron Concentration as function of distance to surface (in pixels)

Figure S7: Iron concentration as function of distance to the surface of the particle. Top: all 19 graphs superimposed. The graphs were normalized to the average of the values for d=100 to 200 pixels from the surface. Bottom: cumulative stacked image (i.e. not a 3D surface plot) using the graphs from the top part illustrating the concentration of iron in a thin outer shell.

The SEM-EDX spectrum recorded from the low-resolution overview image containing all particles also shows the presence of Mn. Based on the peak areas, we conclude that the concentration of Mn is in the same order of magnitude as the Fe concentration (i.e. between 0.5 and 1.0 wt%). Figure S7 shows a detail of the X-Ray spectrum in the range of interest. The marker lines in the spectrum indicate the position and relative intensity of La-spectral lines.

The catalyst contains La, which is introduced in the zeolite active component to increase the thermal stability. Since La has a number of X-ray peaks in the range of interest, we examined the spectrum carefully to exclude the possibility of incorrect assignment due to peak-overlap.

We believe the spectrum below clearly demonstrates the assignment of the Mn-peaks is correct.



Figure S8: Detail of the X-Ray emission spectrum recorded from a low-resolution overview image containing all particles examined in the previous section. The presence of both Fe and Mn, in similar concentrations, is clear from the spectrum. In order to ensure that the intensity assigned to Mn was not caused by overlap with La-peaks, we included the peak positions and relative intensities of the La-lines. The contributions from Ti and Ni (small) result from raw materials in the catalyst and metal deposition during operation, respectively, and are not believed to be relevant for the discussion in this section.

In contrast to Iron, the Mn is not concentrated in the outer shell of the catalyst particles, but rather in small clusters inside the catalyst particles. We performed the same analysis as described above for 17 of the 19 particles (the Mn-images from two particles were not available). The results are shown in Figure S9. These figures clearly show the Mn is, on average, more evenly spread throughout the particles, and certainly not concentrated in an outer shell. From the normalized graphs in the top image of Figure S9, it is clear that some particles have local increased concentrations of Mn inside the particles. The bottom part of Figure S9 again shows a stacked graph constructed from summing the individual graphs, in essence creating a moving average.



Manganese Concentration as function of distance to surface (in pixels)





Figure S9: Manganese concentration as function of distance to the surface of the particle. Top: all 17 graphs superimposed. The graphs were normalized to the average of the values for d=100 to 200 pixels from the surface. Bottom: cumulative stacked image (i.e. not a 3D surface plot) using the graphs from the top part illustrating the more even distribution of Mn compared to Fe.

B. EPR Spectroscopy

EPR spectra were recorded on a Bruker EMX Plus 6000 Gauss instrument with an ER 041 XG Xband microwave bridge at 100 K. Prior to measurements the quartz sample tubes were flushed with N₂. The reported g-values are calibrated for the magnetic field offset using a reference spectrum of BDPA (g = 2.0036).

The resulting full spectrum is shown in Figure S10. A clear signal is observed around g = 4.26, which is attributed to isolated Fe(III) with a pseudo-distorted tetrahedral coordination. Around g = 2.0, three different sets of lines are overlapping. First, the sharp feature (g = 2.002) is assigned to an organic radical, probably originating from the conjugated aromatic coke species. Second, the broad line overlapping with this sharp feature with a g-value around 2.01 is assigned to iron oxide agglomerates. Third, a splitting pattern of 6 spaced lines are observed, of which some are overshadowed by the signal from the organic radical (g = 2.01, A = 68 - 116 G). This pattern indicates the interaction between the electronic and nuclear magnetic moment with a nuclear spin of 5/2 and is therefore assigned to Mn²⁺ [10].

We therefore conclude the majority of the EPR pattern can be explained by contributions from Iron, with a small contribution from Mn superimposed on the largest iron-feature.



Figure S10: EPR spectra.

C. Solid-state NMR Experiments and Analysis

(i) We conducted solid-state NMR experiments at room temperature (293 K) and under low temperature (100 K) DNP conditions using 3.2 mm triple-resonance (¹H, ¹³C, and ¹⁵N) magic-angle-spinning (MAS) probe heads in static magnetic fields of 9.4 and 18.8 T, corresponding to proton/electron resonance frequencies of 400 MHz/263 GHz and 800 MHz/527 GHz (Bruker BioSpin, [11]), respectively. DNP samples were prepared by wetting [12, 13], using a solution of 15mM Pypol [14] in tetrachloroethane. The ssNMR experiments presented in Figures 1-3 were obtained using the following experimental parameters:

	Number of	CP-contact time	Relaxation delay
	scans		
Figure 1A	1024	2ms	2sec
Figure 1B	384	50µs	2sec
Figure 2	1024	2ms	2sec
Figure 3 RT	40960	2ms	2sec
(with and			
without radical)			
Figure 3 LT	40960	2ms	2sec
(without radical)			
Figure 3 RT	1024	2ms	2sec
(with radical)			

Table S3 experimental parameters used for Figures 1-3

All spectra were recorded at a MAS rate of 8 kHz using 83 kHz SPINAL-64 proton decoupling [15], unless mentioned otherwise. The spectrum shown in Figure 1B was recorded using 88 t_1 points. Processing was done in TOPSPIN 3.5 with QSINE=2 and 1024 zero-filling. FSLG [16] were established using an offset of 58kHz and an ¹H radiofrequency field strength of 83kHz.

(ii) DNP enhancements were obtained by scaling the signal intensities of spectra measured under DNP with the corresponding spectrum obtained without microwave irradiation at 100K using 8kHz MAS.

(iii) Spinning sidebands were identified by varying spinning speeds at 400 and 800 MHz as shown in Figure S11:



Figure S11: ¹³C CP-MAS spectra measured with DNP at 100 K using various spinning speeds. The NMR spectra in panel A were measured at 400 MHz, while the NMR spectra in panel B were measured at 800 MHz. The asterisks represent the identified spinning side-bands.

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