Time-resolved *in situ* studies on the formation mechanism of iron oxide nanoparticles using combined fast-XANES and SAXS

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Supplementary Information

S1) Simulation of XANES data using FEFF:

In the present work the FEFF9¹ code has been used to model the experimental XANES data. The aim is to obtain information about density of states unoccupied, chemical species, and oxidation state theoretically and compare it with the experimental data.

In the region of the pre-edge dipolar and quadrupole transitions take place.² In the case of quadrupole transitions the intensity of the pre-edge peak can be increased, when the electric field has a particular direction. This does not happen in the case of dipole transitions, where a weak pre-edge peak is observed.

Figure S1 shows the comparison between experimentally measured FeCl₃·6 H₂O molecule (solid black line), pure quadrupole transitions (1s \rightarrow 3d) (dashed black line), and both transitions possibilities (dipolar (3d-4p mixing) and quadrupole transitions (grey line)) simulated with the FEFF9 code.³ When a pure quadrupole transitions is simulated, a strong pre-edge peak occurs. When compared with the measured spectrum (solid black line), the pre-edge peak is a result of mixed transitions, which indicates an octahedral coordination geometry of iron. Furthermore, the integrated pre-edge peak area and height of the pre-edge peak are directly correlated. Therefore, the integrated peak area (IPA) will be used for data evaluation.



Figure S1: XANES spectra of FeCl₃·6 H₂O experimentally measured (solid black line) together with both FEFF simulations. In grey both, quadrupole and dipole transitions, are considered. In dashed black only pure quadrupole transition is considered.

S2) Evaluation of the SAXS data:

The small-angle scattering curves were fitted using the unified fit described by Beaucage *et al.*.⁴ In this function, the particle radius, in terms of the radius of gyration derived from Guiniers law, and the particle surface scattering in the Porod regime are directly combined.

For a single polydisperse level of structure the unified fit function is written as:

$$I(q) = G \exp\left(\frac{-q^2 R_g^2}{3}\right) + B\left(\frac{q}{\left[erf\left(qR_g/\sqrt{6}\right)\right]^3}\right)^{-4}$$

where erf() is the error function. G is given by $G = Nr_e^2 \rho_e^2 V^2$, where N represents the total number density of primary particles, r_e is the classical electron radius, ρ_e the electron density difference, and V the average particle volume. B is given by $B = 2\pi N r_e^2 \rho_e^2 S$, where S is the average surface area of the primary particles.

S3) Additional SAXS measurements:



Figure S3: a) SAXS scattering curves as a function of time at an excitation energy of 12 keV. Spectrum taken one minute after the addition of TREA is marked in black. Spectra taken shortly after the addition of TREA are marked by a colour change from dark red (4 min) to light green (91 min) b) Evaluation of the radius of gyration at an excitation energy of 12 keV as a function of time. No evaluation of a radius of gyration was possible until a reaction time of 4 min. The dashed line at 0 min visualizes the addition of TREA to the heated iron chlorides. The light and dark grey shaded backgrounds illustrate different changing stages during the reaction.

The SAXS data, which were performed at 12 keV with a better time resolution, confirm the reaction trend. The small particles already occur 4 min after the addition of TREA and growth to particles with a radius of gyration of 3.9 nm.

The obtained synchrotron based SAXS data were confirmed with the SAXS data received by a laboratory SAXS instrument (SAXSess, Anton Paar, Graz, Austria) equipped with a sealed X-ray tube (Cu anode target, $\lambda = 1.5406$ Å), with a lower q-range (0.08 nm⁻¹). The maximal object size that can be determined corresponds to d_{max} = $\pi/q_{min} = 39$ nm. A mean radius of gyration of 3.9 nm was obtained from three independent experiments (3.7 nm, 4.1 nm, and 3.9 nm).

S4) XRD and ESEM of akaganeite:



Figure S4: Characterization of akaganeite, after heating the iron chloride solution. a) XRD analysis of the precipitate in comparison to the JCPDS *database* entry (*PDF*: 42-1315) for the iron oxide hydroxide akaganeite (red). The intermediate phase was analyzed directly in reaction solution by XRD. The diffraction pattern shows sharp peaks. XRD analysis in solution was performed at the μ Spot beamline using the same setup as described for the SAXS measurements at a sample-detector distance of 151.6 mm. b) ESEM measurements of the dried precipitate (scale bar 5 μ m).

5) Raman analysis:



Figure S5: Raman spectra as a function of time. The heated ferric and ferrous chloride solution is marked in red. The Raman spectra measured 1 min after the addition of TREA is marked in black. Spectra taken 7 min after the addition of TREA are marked by a colour change from dark red (7 min) to light green (91 min, final nanoparticles). The blue spectrum is attributed to the TREA/water mixture. The dashed line at 669 cm⁻¹ symbolizes the position of the magnetite signal. The dashed line at 310 cm⁻¹, 390 cm⁻¹ and 720 cm⁻¹ symbolize the position of the akaganeite signal.

The Raman spectra of the final NPs is dominated by the bands of TREA.⁵ Prior the addition of TREA, the heated ferric and ferrous chloride solutions show broad signals at 310 cm⁻¹, 390 cm⁻¹ and 720 cm⁻¹, which can be attributed to akaganeite.⁶ No signal occurs at 669 cm⁻¹, indicating the absence of magnetite Fe₃O₄ as dominant phase (670 cm⁻¹, A_{1g} mode). The signal of the A_{1g} mode of maghemite γ -Fe₂O₃ should occur between 700-720 cm⁻¹.^{7,8} This feature could be superimposed by the signal of TREA. Therefore, the main phase of the synthesized final iron oxide nanoparticles is maghemite. The evaluation of the Raman data 7 minutes after

the TREA addition shows a signal at 669 cm⁻¹, which indicates the presence of magnetite as dominant phase.



S6) XANES spectra of chloride mixtures:

Figure S6: a) Normalized XANES spectra of iron chloride mixtures with different fractions of Fe^{3+} ($F_{Fe}^{3+} = 0$ (pure Fe^{2+}) – 1 (pure Fe^{3+})) in solution. The spectra are background corrected. The spectra are marked by a colour change from dark red ($F_{Fe}^{3+} = 0$) to light green ($F_{Fe}^{3+} = 1$) by increasing the fraction of Fe^{3+} . b) Normalized pre-edge peak XANES spectra of iron chloride mixtures for different fractions of ferric chloride ($F_{Fe}^{3+} = 0$ to 1) in solution. The spectra are background corrected. With increase of the fraction F_{Fe}^{3+} , the XANES spectra are marked by a colour change from red to light green. The arrows visualize the changes of the pre-edge peak height by increasing the fraction F_{Fe}^{3+} .

In Figure S6, the normalized pre-edge peak XANES spectra of iron chloride mixtures with different fractions of ferric chloride ($F_{Fe}^{3+} = 0$ to 1) in solution are presented. The pre-edge peak for $F_{Fe}^{3+} = 0$ (Fe²⁺) and $F_{Fe}^{3+} = 1$ (Fe³⁺) show pronounced intensity. The signal becomes broader and decreases in intensity for mixtures (Figure S6b). In solution, the area of the pre-edge peak for $F_{Fe}^{3+} = 0$ (pure Fe²⁺) is smaller compared to the mixtures with higher Fe³⁺ content. This feature can be attributed to the decreasing number of d electrons in pure Fe³⁺ compared to pure Fe²⁺.⁹

S7) SAED pattern of the nanoparticles (7 minutes after the addition of TREA):



Figure S7: SAED data of the small nanoparticles with a R_G = 3 nm. The XRD pattern fits with the XRD pattern of the iron oxide nanoparticles with a spinel structure (maghemite or magnetite).



S8) Time-resolved XANES data of experiment type 2:

Figure S8: XANES data as a function of time for experiment 2 (0.125 M HCl solution as iron precursor solution). *In situ* XANES data (Fe K-edge) as a function of time. Spectra of the iron chloride solution and those obtained during heating are marked in grey. The spectrum taken one minute after the addition of TREA is marked in black. Spectra taken shortly after the addition of TREA are indicated by a colour change from dark red (7 min) to light green (91 min).

References:

- 1 J. J. K. J.J. Rehr, F.D. Vila, M.P. Prange, K. Jorissen Phys. Chem., 2010, 12, 5503.
- 2 R. C. A. J. J. Rehr Reviews of Modern Physics, 2000, 72, 621.
- 3 T. E. Westre; P. Kennepohl; J. G. DeWitt; B. Hedman; K. O. Hodgson; E. I. Solomon *Journal of the American Chemical Society*, 1997, **119**, 6297.
- 4 G. Beaucage Journal of Applied Crystallography, 1995, 28, 717.
- 5 D. B. Salvi; H. Barud; A. Pawlicka; R. Mattos; E. Raphael; Y. Messaddeq; S. L. Ribeiro *Cellulose*, 2014, 1.
- 6 L. Bellot-Gurlet; D. Neff; S. Réguer; J. Monnier; M. Saheb; P. Dillmann *Journal of Nano Research*, 2009, **8**, 147.
- 7 D. L. A. deFaria; S. V. Silva; M. T. deOliveira Journal of Raman Spectroscopy, 1997, 28, 873.
- 8 I. Chamritski; G. Burns The Journal of Physical Chemistry B, 2005, 109, 4965.
- 9 T. Yamamoto X-Ray Spectrometry, 2008, **37**, 572.