Supplementary Materials for Coagulating and flocculating Ferrihydrite: Application of Zinc Acetate salt

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EXAFS details

X-ray absorption spectra at the Fe (E_o=7112 eV) was collected at the XAFS beamline of the Elettra synchrotron radiation center (Trieste, Italy) in transmission geometry keeping the samples at room temperature. The near edge (XANES) and extended (EXAFS) features were quantitatively providing information about the average valence state and ligand symmetry around the Fe absorber and the further precise details about the coordination chemistry in terms of neighbour coordination shells, respectively. X-ray absorption spectra were also measured on reference samples for sake of comparison (pure Fe, 2L-Fh_{ref}).

The centroid position C_p, and area A_p, of the pre-edge peak in the Fe XANES spectra of iron oxides can provide detailed information about the valence state and average Fe-O coordination number[1,2] We found A_p of 2L-Fh to be 17-18 eV and C_p for 2L-Fh being about 2.3-2.4 eV above the Fe *K*-edge (the Fe-metal foil *K*-edge energy was used for calibration), consistent with the A_p(Fh-$2L_{ref}$)~19 eV and C_p(Fh-$2L_{ref}$)~2.4 eV obtained for the pre-edge XANES peak of the reference Ferrihydrite sample. These values are consistent with average 5 coordinated Fe(III) atoms, pointing out a combination of octahedrally coordinated FeO_6 and tetrahedrally coordinated FeO_4 ions. The k^2 weighted experimental EXAFS spectra of 2L-Fh, and 2L-Fh_{ref} are presented in Fig. S-1 along with the best fit curves for sake of comparison. The two experimental spectra depict very similar features strengthening once more the Ferrihydrite nature of the precipitate powders. Multi-shell data fitting procedure has been firstly tuned refining the 2L-Fh_{ref} EXAFS spectra starting from the Ferrihydrite structure proposed, based on Pair Distribution Function analysis.[3] Data refinement requires two Fe-O1,2 and three Fe-Fe1,2,3 shells (As shown in Table S-1, the Fe-Oi and Fe-Fei distances are in agreement with the proposed theoretical model). The same contributions were used to fit 2L-Fh (As shown in Table S-1), however the statistical analysis indicates that only three contributions are significant to fit the spectra: Fe-O1, Fe-Fe1 and Fe-Fe3. The Fe-O2 is definitively weak in the 2L-Fh_{ref}, therefore it could be hindered by larger structural disorder in the precipitated samples. The coordination numbers of Fe-Fei contributions depict strong correlation owing to the effect of anti-phase EXAFS oscillations. This correlation, coupled with the higher structural disorder may hinder a more complex distribution of Fe-Fe neighbour in the analysis.

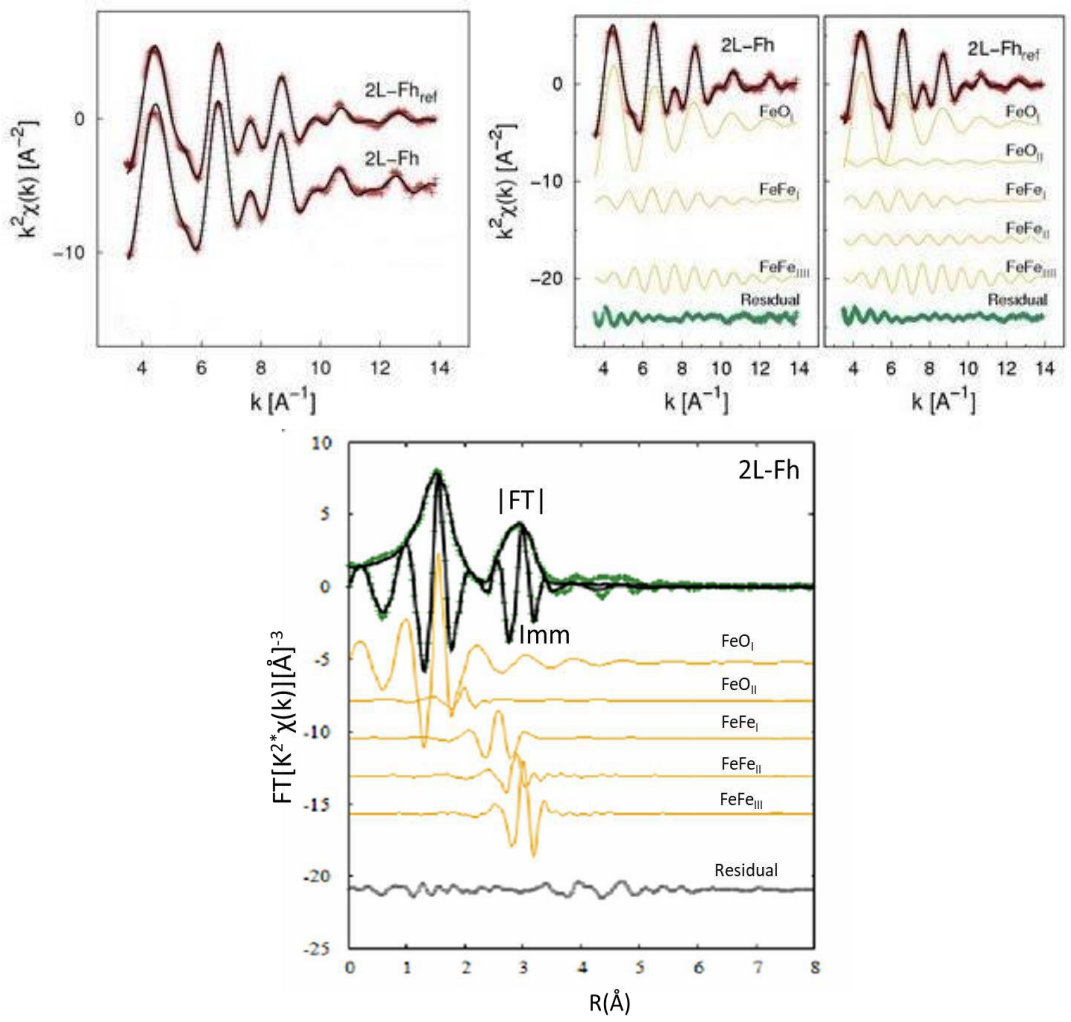

Fig. S-1: Fe *K*-edge EXAFS data and their analysis: Left top panel: EXAFS data of 2L-Fh and 2L-Fh$_{ref}$ for comparison; Top right panels: Contributions considered for fitting of these data; Bottom panel: Real space distances and contributions from the 2L-Fh sample.

Table S-1: Fe *K*-edge XAFS data analysis results along with theoretical calculation results (shown in square bracket)

	2L-Fh$_{ref}$			2L-Fh		
	A_p (eV)		**C_p(eV)**	**A_p (eV)**		**C_p(eV)**
	19.1(8)		2.36(7)	17.6(8)		2.33(7)
	N	**R(Å)**	**σ^2(x10^{-3})**	**N**	**R(Å)**	**σ^2(x10^{-3})**
Fe-O$_1$	4.9(3)	1.912(8) *[1.93]*	11.(1)	5.06(20)	1.939(6)	9.4(6)
Fe-O$_2$	0.5(2)	2.36(2) *[2.15]*	5.2(4)	-		
Fe-Fe$_1$	2.0*	2.98(1) *[3.15]*	16.(2)	1.8(4)	2.99(2)	12(1)
Fe-Fe$_2$	1.5*	3.25(2)	2.9(3)	-		
Fe-Fe$_3$	2.0*	3.40(2) *[3.60]*	7.4(3)	2.3(2)	3.42(2)	8.7(7)

Theoretical Methodology

The electronic structure studies for all clusters and related species were performed using density functional theory (DFT) as implemented in the Gaussian 09 suite of programs.[4] Studies were performed using the B3LYP[5-7] hybrid functional with the 6-31G** basis sets for all atoms. The stable clusters were determined by full geometry optimization in the gas-phase and consequent harmonic frequency calculations were performed to ascertain the stationary points. Gas phase enthalpies and Gibbs free energies were computed by adding enthalpy corrections and Gibbs free energy corrections respectively to the total energies at 298K and 1 atm pressure from gas phase frequency studies.

In this case, the δ-Fe_{13} cluster has been studied only in the high-spin configuration (Spin-multiplicity M_s: 2S+1=66), as low spin structures could not be stabilized using DFT. However in case of smaller Fe(III) oxyhydroxide clusters the Fe-Fe bond distances were smaller by 0.2-0.3 Å for the low-spin cases and the overall size of the clusters were more compact[8].

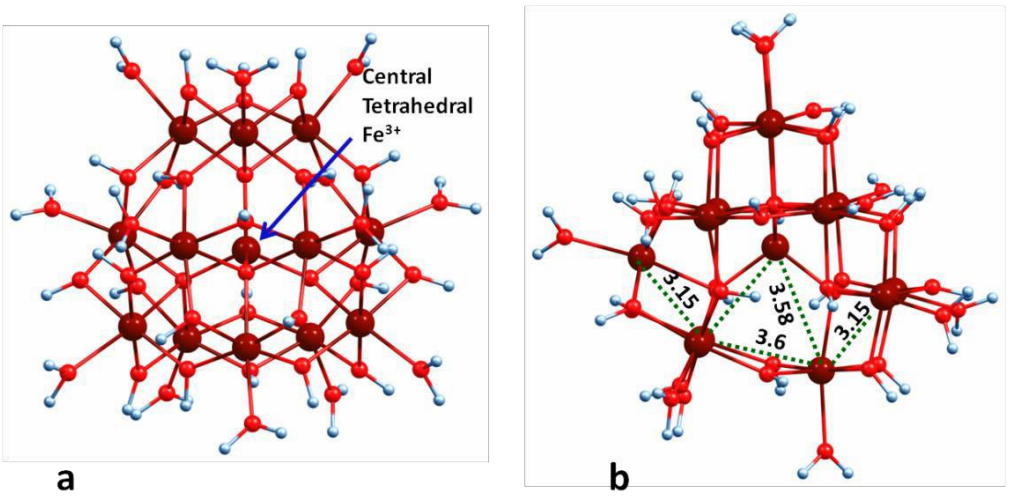

Fig. S-2:(a) δ-Fe_{13} Keggin cluster $[FeO_4(Fe(OH)_2(H_2O))_{12}]^{7+}$, $(Fe_{13}H_{48}O_{40})^{7+}$ (b) Two types of non-bonded Fe-Fe distances in Ă are shown in a rotated view of δ-Fe_{13} Keggin cluster for better clarity. In the figure the biggest brown balls are Fe, medium red balls represent O and small bluish balls are H.

Optimized Cartesian co-ordinates for δ-Fe_{13} Keggin cluster:

Fe_{13}Keggin ion cluster

B3LYP/6-31G**, charge:+7, M_s; 66, E:-19462.852641 H, H=-19462.754778 H, G: -19462.974923 H

O	1.748789000	-0.446288000	-0.797018000
O	-1.460831000	-0.890444000	-0.964579000
O	-0.250531000	1.968114000	-0.271906000
O	-0.021956000	-0.585744000	1.753219000
O	2.724114000	2.344061000	-0.115529000
O	-4.090575000	-1.196898000	-0.824798000
O	-2.495127000	-1.084744000	-3.356368000
Fe	-0.494243000	2.958777000	1.615304000
Fe	-1.737333000	-0.152204000	3.007887000
Fe	1.372866000	0.237073000	3.174708000
O	0.401000000	-1.410519000	-3.565233000
O	3.096865000	-0.336797000	-3.060043000
O	1.943477000	2.217886000	-2.456113000
Fe	0.179717000	-2.511151000	2.427440000
Fe	3.093531000	-1.474729000	0.454992000
Fe	2.012494000	-1.880637000	-2.490724000
O	-2.152606000	1.669352000	-2.692885000
O	-3.207024000	1.543992000	-0.458576000
O	-2.293824000	-3.369119000	-1.465146000
Fe	3.166884000	0.946318000	-1.541390000
Fe	-3.101582000	0.106455000	-1.910766000

Fe	-1.111266000	-2.288455000	-2.623134000
O	-2.992792000	-1.029648000	1.667474000
O	-1.196178000	-3.204194000	1.125967000
O	-0.400740000	3.914332000	-2.034643000
Fe	-2.667683000	-2.251173000	0.148103000
Fe	-1.913112000	2.947837000	-1.210074000
Fe	1.203279000	3.365090000	-1.026896000
O	-1.960252000	3.853657000	0.532840000
O	0.804772000	4.219177000	0.699872000
O	-1.878796000	1.589061000	2.072748000
O	1.124983000	1.985050000	2.248856000
O	-0.310072000	0.613808000	4.129171000
O	-1.340681000	-1.991171000	3.628914000
O	1.357308000	-1.668884000	3.788385000
O	2.917629000	-0.239319000	1.990927000
O	1.716318000	-2.768352000	1.148045000
O	3.296702000	-2.610623000	-1.166146000
O	4.328512000	-0.060999000	-0.323558000
O	0.546841000	-2.947926000	-1.736496000
H	0.360294000	-0.889084000	-4.378674000
H	3.796681000	-0.367540000	-3.731208000
H	1.592592000	2.108863000	-3.350738000
H	3.473791000	2.886029000	0.180687000
H	-4.887078000	-1.665719000	-1.117843000
H	-3.009579000	-1.305755000	-4.148637000
H	-1.680352000	1.668745000	-3.536771000
H	-4.102562000	1.869451000	-0.269484000
H	-2.455443000	-4.315918000	-1.588804000
H	-3.821250000	-0.557976000	1.484742000
H	-1.108370000	-4.123589000	0.832697000
H	-0.489232000	4.762703000	-2.497500000
H	-2.170067000	4.790854000	0.662692000
H	0.746336000	5.176489000	0.839469000
H	-2.518923000	1.593707000	1.327002000
H	1.834714000	2.183649000	1.600194000
H	-0.403671000	0.725103000	5.087731000
H	-2.075276000	-2.617642000	3.713114000
H	1.058086000	-1.820304000	4.700496000
H	3.612876000	0.432918000	1.910055000
H	2.097612000	-3.661180000	1.183731000
H	4.120473000	-3.019223000	-1.472690000
H	5.276749000	-0.230503000	-0.431958000
H	0.616507000	-3.257589000	-0.819910000
Fe	0.002885000	0.041251000	-0.096049000
O	4.729077000	-2.501027000	1.385626000
H	5.050918000	-2.281748000	2.276283000
H	5.303133000	-3.213738000	1.055254000
O	2.832168000	-3.220303000	-3.933371000

H	2.944221000	-4.177058000	-3.794576000
H	3.112149000	-3.041166000	-4.848115000
O	4.893316000	1.933994000	-2.343499000
H	5.820931000	1.880366000	-2.054638000
H	4.890589000	2.494808000	-3.137746000
O	-4.928090000	0.614250000	-2.905020000
H	-4.992206000	1.109600000	-3.739451000
H	-5.834427000	0.335740000	-2.686378000
O	-1.387330000	-3.680957000	-4.196291000
H	-0.796660000	-3.784738000	-4.960837000
H	-2.106955000	-4.323843000	-4.319366000
O	-4.195316000	-3.643336000	0.768852000
H	-4.735053000	-3.540514000	1.570764000
H	-4.553459000	-4.419285000	0.304160000
O	-3.354944000	4.324206000	-1.978328000
H	-3.872778000	4.989452000	-1.492004000
H	-3.574295000	4.445763000	-2.918252000
O	2.309236000	5.090652000	-1.635401000
H	2.572248000	5.303180000	-2.547606000
H	2.590343000	5.846703000	-1.090793000
O	-0.764137000	4.274605000	3.232991000
H	-1.610677000	4.532690000	3.636649000
H	-0.063758000	4.734017000	3.727580000
O	-3.220932000	0.164979000	4.478024000
H	-3.437958000	-0.446955000	5.203611000
H	-3.743411000	0.970874000	4.629971000
O	2.612008000	0.876843000	4.754424000
H	3.207494000	0.301676000	5.266291000
H	2.651377000	1.757184000	5.165848000
O	0.521866000	-4.458921000	3.264161000
H	-0.114586000	-5.183347000	3.396793000
H	1.242570000	-4.626352000	3.897288000

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