Supporting information

The effect of Mo and V on the hydrothermal crystallisation of hematite from ferrihydrite - an *in situ* Energy Dispersive X Ray Diffraction and X Ray Absorption Spectroscopy study

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Number of pages: 6

Number of figures: 7

Results

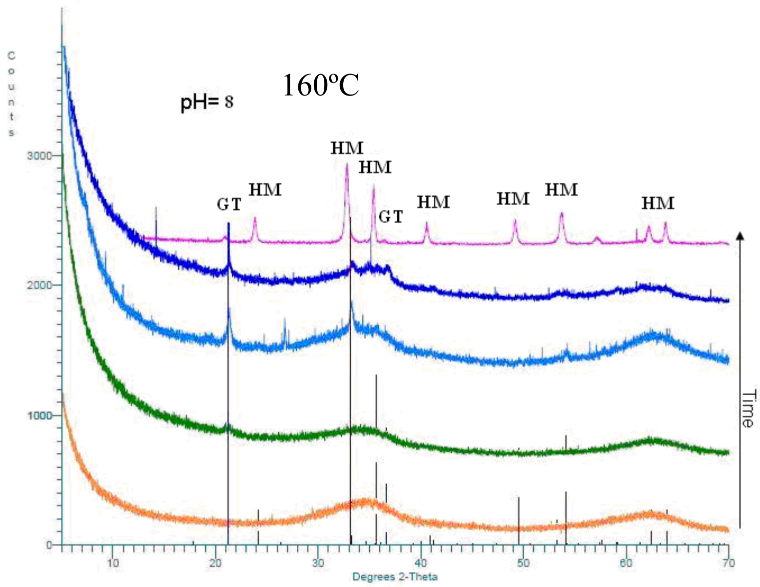


Figure SI 1. XRD patterns from off-line experiments, corresponding to TEM imaging in Figure 1:), supporting that transformation of ferrihydrite (FH) to hematite (HM) occurs with minor amounts of goethite (GT)

XRD data interpretation was done using the following JCPDS-ICDD cards: 29-712 for 2 line ferrihydrite, 29-713 for goethite and 33-664 for hematite. The Bragg 110 hematite and goethite peaks were chosen as a distinct peak with high intensity which can differentiate hematite from goethite in the mixed phases[1, 2].

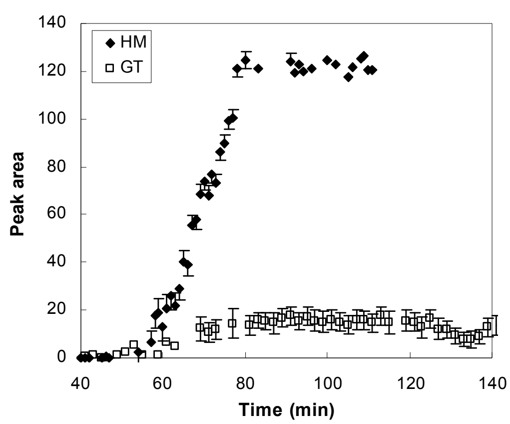


Figure SI 2. Progresion of hematite (110) and goethite (110) peak areas as function of time for FH-Mo system from in situ transformation experiment, at 140ºC and IS 0.7, indicating that small proportions of goethite [GT (110)] is formed besides hematite [HM (110)]. From differences in GT *vs.* HM peaks area, it can be noticed that goethite is a minor phase (also note large error for GT

110 peak) and that it fully disappeared at the end of the reaction with hematite remaining the sole end-product.

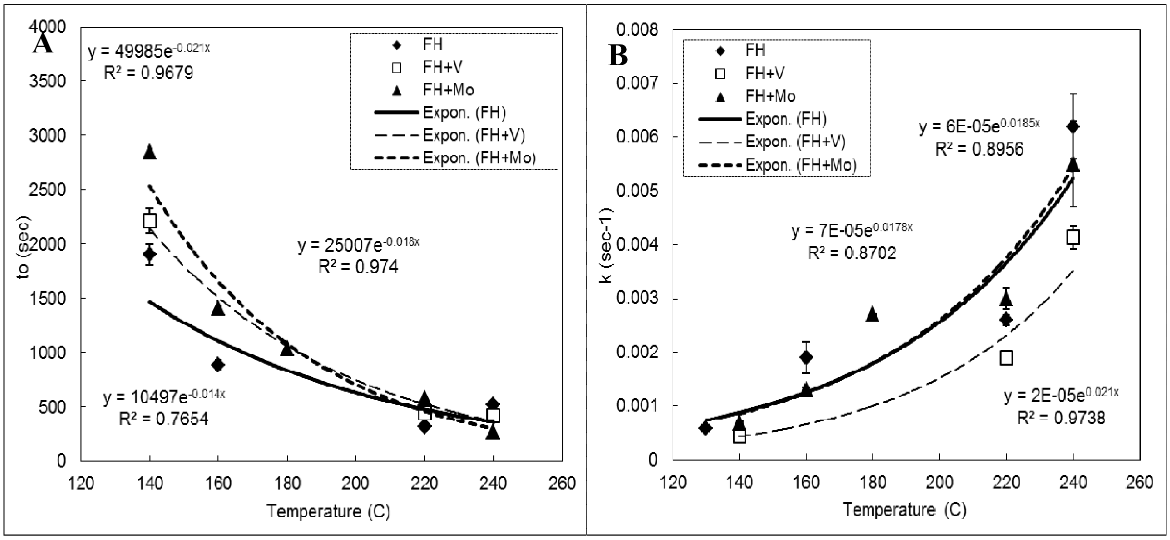


Figure SI 3. The profiles of induction times (A) and rates constant (B) and as a function of temperature for the three studied systems (hematite crystallisation in the presence and absence of Mo and V) illustrating that in all systems the crystallisation induction times increase with decreasing temperature while the crystallisation rates increase with increasing temperature. The data were best fitted to an exponential polynomial.

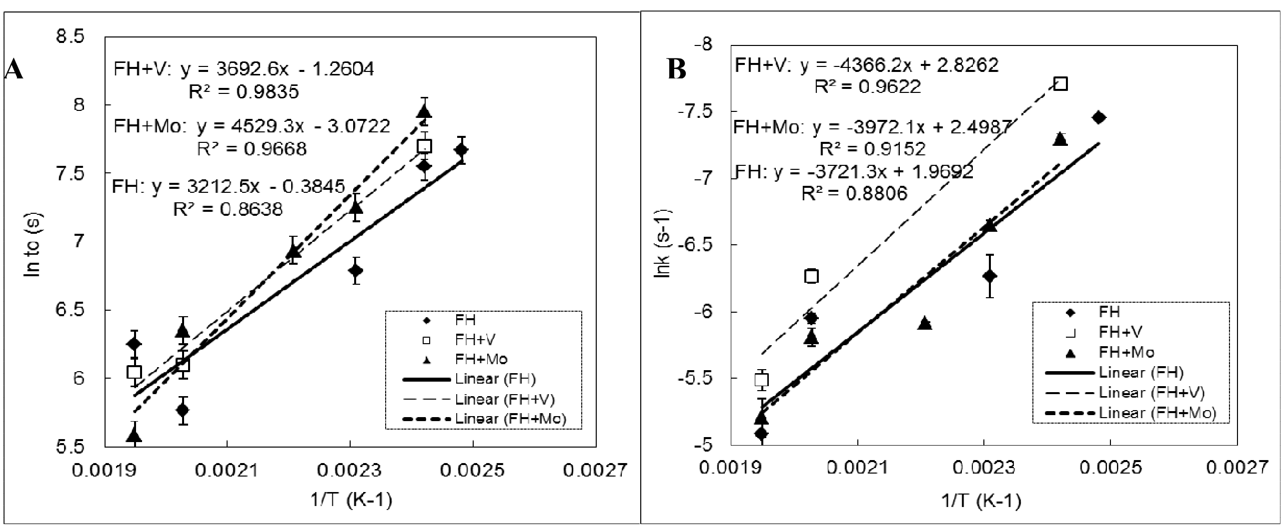


Figure SI 4. Arrhenius plots for (A) induction time, t_o and (B) rate of growth, k, of HM crystallisation in the three studied systems.

Figures SI 3 and SI 4 are important for calculation the time of induction, transformation rates to any given temperatures via extrapolation.

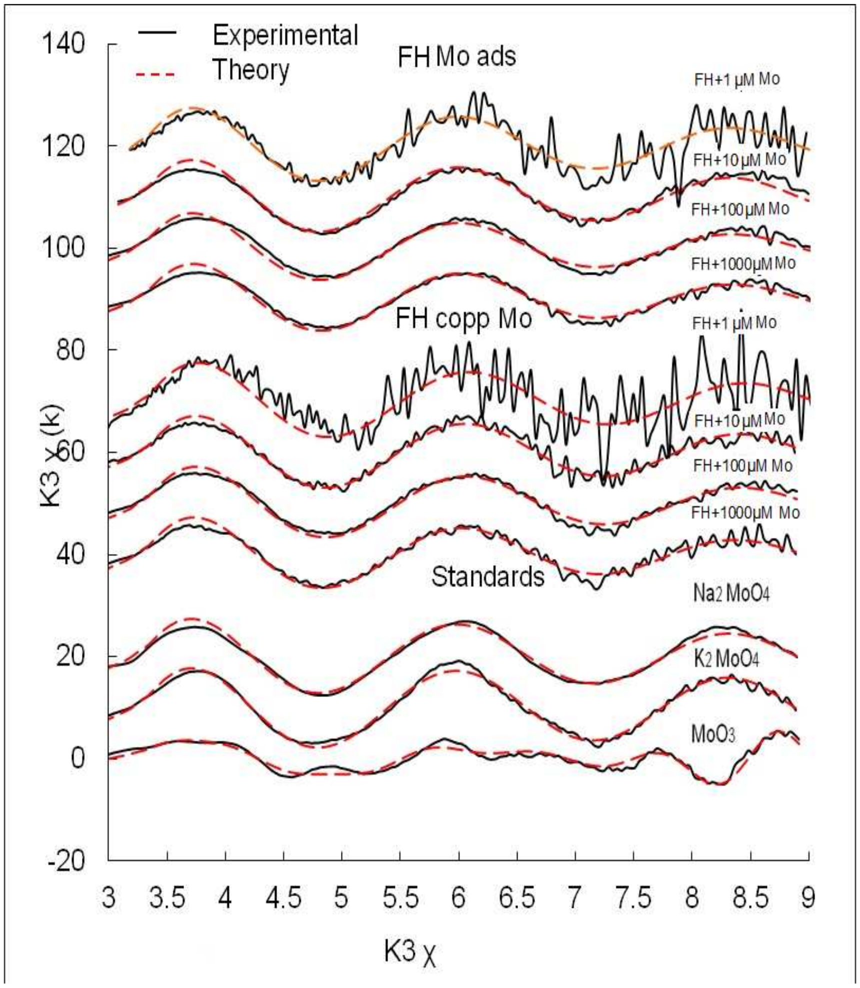


Figure SI 5. Mo k^3 weighted EXAFS spectra for ferrihydrite adsorbed (top spectra) and co-precipitated (middle spectra) experiments at different Mo concentrations and standards (bottom spectra) showing that spectra are alike for all molybdenum doping concentrations, indicating that molybdenum did not form specific precipitates or polymerized during co-precipitation/adsorption experiments.

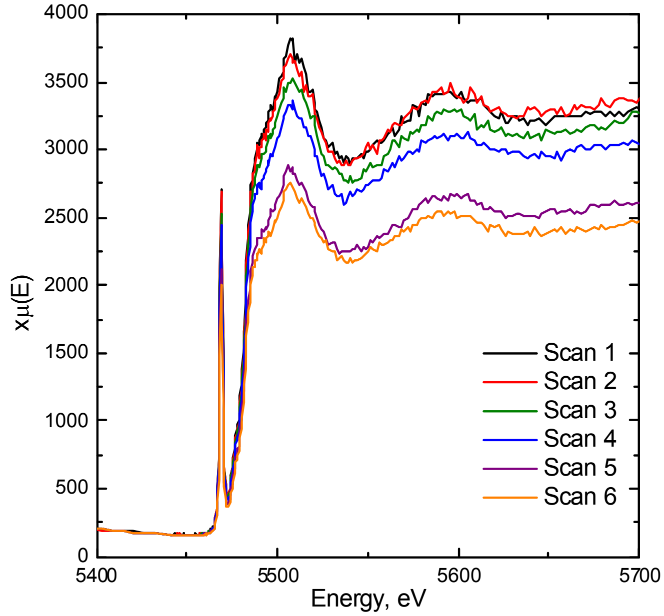
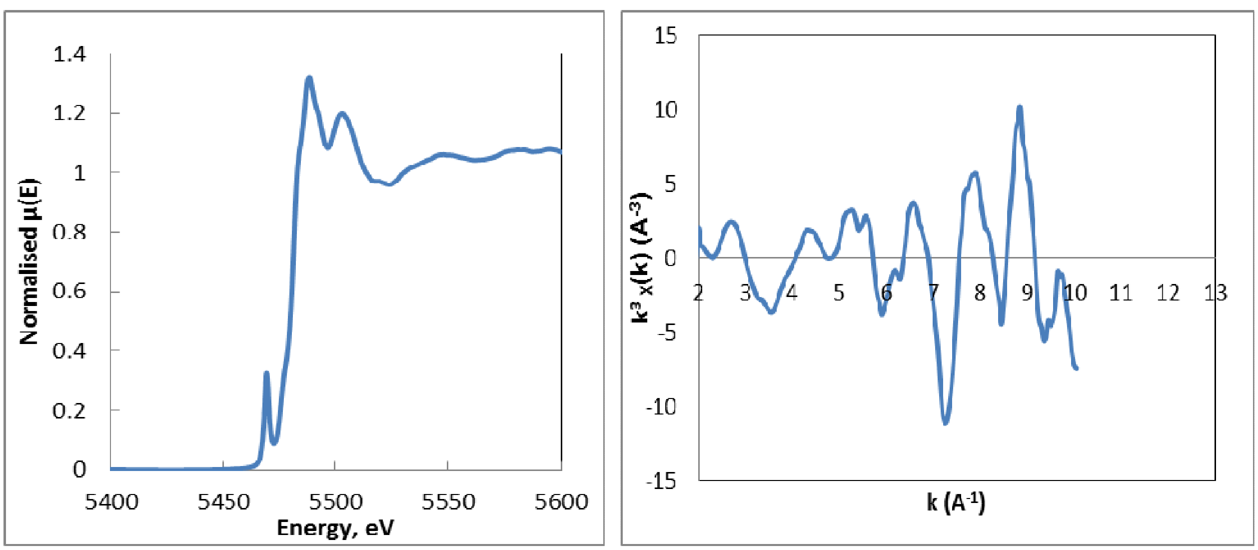


Figure SI 6. Non normalized V-XANES showing beam dehydration effect of V co precipitated fresh ferrihydrite (sample run at room temperature).



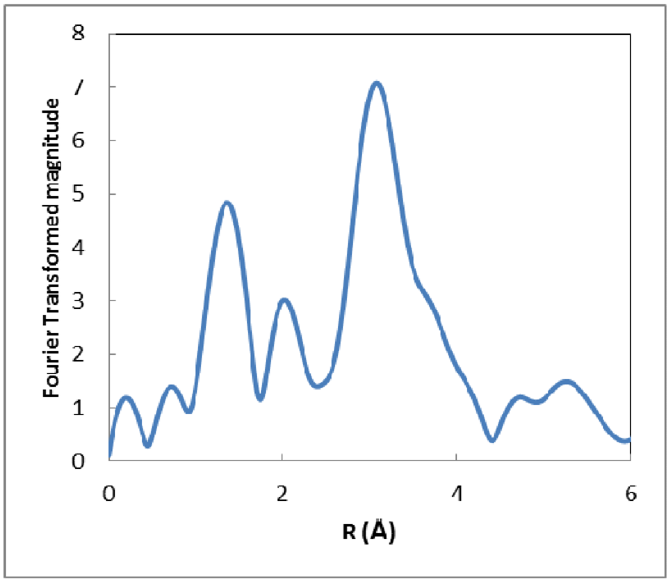


Figure SI 7. Normalized XANES (A), splined K3 weighted EXAFS (B) and FT of EXAFS (C) spectra of V in V-copp- tr sample, showing that V bonding environment in transformed sample has changed, but to our best try no sensible model could be fitted, thus we included the data for possible future references.

(1) Vu, H. P.; Shaw, S.; Brinza, L.; Benning, L. G., Crystallization of Hematite (alpha-Fe_2O_3) under Alkaline Condition: The Effects of Pb. *Crys. Growth Des.* **2010,** 10, 1544-1551.

(2) Murray, J.; Kirwan, L.; Loan, M.; Hodnett, B. K., In-situ Synchrotron Diffraction Study of the Hydrothermal Transformation of Goethite to Hematite in Sodium Aluminate Solutions. *Hydrometallurgy* **2009,** 95, 239-246.