Supporting information for "Mapping the redox chemistry of common solvents in solvothermal synthesis through *in situ* X-ray diffraction"

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Details for Rietveld refinements

Rietveld refinements were performed using the Fullprof software package.¹ Scale factor, unit cell parameter(s) and zero displacement parameter were all refined. The Thompson-Cox-Hastings pseudo-Voigt formulation of peak shape was used, and broadening parameters chosen so that the best description was obtained using only one or two parameters. The remaining parameters were set to zero. The average crystallite size was extracted *via* the Fullprof micro-structural analysis when feasible (peak broadening was described by parameters Y or I_G). All B-values (describing thermal motion) were set to 0.8 Å² as a rough estimate since the experiments span a wide temperature range and the data quality is insufficient for reliable refinements of these. The instrumental broadening was accounted for by Rietveld refinements of NIST LaB₆ 660b line profile standard data measured in identical experimental geometry. Backgrounds were modelled using linear interpolation between points with refinable heights.

Copper in 10% hydrogen peroxide solution

At 200 °C peaks belonging to an unidentified phase appear. These are replaced by peaks from copper(II) oxide (ICSD 16025) at 300 °C, at which temperature a partial reduction to copper(I) oxide (ICSD 63281) also starts. At 450 °C, only copper(I) oxide remains.



Cu(NO₃)₂ in Hydrogen Peroxide @ 400 °C: CuO (tenorite) + Cu₂O



Cu(NO₃)₂ in Hydrogen Peroxide @ 450 °C: Cu₂O



Copper in water

No crystalline phase was observed during the heating steps. When probing other volumes of the reactor capillary (marked with red dashed line), Bragg peaks belonging to copper(II) oxide (ICSD 16025, $R_f = 7.74$) were observed.



Copper in ethanol

The following phases were refined: Rouaite (COD 9008310, $R_f = 12.3$), copper(I) oxide (ICSD 63281, $R_f = 20.0$), and metallic copper (ICSD 627114, $R_f = 1.53$). Rouaite was observed to sediment slowly from the precursor, and data was measured on a concentrated suspension of the precipitate ($R_f = 1.89$, see below, titled "copper nitrate in Ethanol precipitate"). As described in the article, rouaite does not match the phase observed at 200 °C perfectly. The phase is believed to have the same parent motif as rouaite, but with minor temperature-induced changes to its symmetry.





Copper in ethylene glycol

Copper(I) oxide (ICSD 63281, $R_f = 18.4$) is formed with a reaction temperature of 200 °C and disappears again at 400 °C where metallic copper (ICSD 627114, $R_f = 1.58$) is observed. An intense low-angle peak and additional minor peaks in the experimental diffractograms for copper(I) oxide is not accounted for by the structure. The growth and decay of the additional peaks follows the growth of the indexed peaks, and it is likely that all peaks stem from the same phase; copper(I) oxide with lowered symmetry.



Copper in glycerol

Copper(I) oxide (ICSD 63281, $R_f = 12.5$) forms at 200 °C and disappears again at 300 °C. Reduction to metallic copper (ICSD 627114, $R_f = 0.807$) starts at 200 °C, and after increasing the temperature to 300 °C only scattering from metallic copper is observed. As observed when using ethylene glycol as solvent, the fit for copper(I) oxide is inadequate with undescribed peaks.



 $Cu(NO_3)_2$ in Glycerol @ 200 °C: Cu_2O





Nickel in 10% hydrogen peroxide solution

No Bragg peaks are observed until 400 °C is reached and nickel(II) nitrate hydroxide, $Ni_3(NO_3)_2OH_4$ (ICDD PDF4+ 00-022-0752) is found to crystallize. Since only peak positions and intensities are reported for the phase, Rietveld refinement was not possible. Peak positions and relative intensities however match data well (red markers, data is blue). Nickel(II) oxide (ICSD 9866, $R_f = 0.619$) start to form after approx. 4 minutes at 400 °C.



Nickel in water

No Bragg peaks were observed during the heating steps, but weak scattering from nickel(II) nitrate hydroxide, $Ni_3(NO_3)_2OH_4$ (ICDD PDF4+ 00-022-0752), was seen when other capillary positions was probed.



Nickel in ethanol

Nickel(II) nitrate hydroxide, Ni₃(NO₃)₂OH₄ (ICDD PDF4+ 00-022-0752), is formed at 200 °C. When heating to 300 °C, the intensity of this phase starts to decrease while peaks from nickel(II) oxide (ICSD 9866, $R_f = 1.32$) appear and grow.



Nickel in ethylene glycol

Above 300 °C, a weakly scattering layered phase is observed. Phase identification was unsuccessful due to peak broadening, but a reasonable candidate is a nitrate hydroxide. At 450 °C, peaks from metallic nickel (ICSD 646092, $R_f = 1.81$) start emerging, and intense peaks are found when probing different capillary positions.



Nickel in glycerol

At 300 °C weak scattering from an unidentifiable phase is observed. Reaching 400 °C, hexagonally closed packed metallic nickel forms (ICDD 04-002-8298, $R_f = 1.96$). Increasing the temperature just 50 °C, an allotropic transformation to face centered cubic metallic nickel (ICSD 646092, $R_f = 1.07$) occurs while a minor fraction of nanosized nickel(II) oxide (ICSD 9866, broadened Bragg peaks, refined to 3.2 nm, $R_f = 1.75$) is also present.



Ni(NO₂)₂ in Glycerol @ 450 °C: Metallic Ni (fcc) + NiO

н

10

2θ (°)

Data Model Difference Background

12

Peak positions

Cobalt in 10% hydrogen peroxide solution

The spinel Co_3O_4 (COD 9005895, R_f = 3.18) forms at 300 °C. After cooling (blue dashed lined, approx. 25 min.), the phase remained stable.



Cobalt in water

The spinel Co_3O_4 (COD 9005895, $R_f = 9.89$) was formed in all experiments. Please note that the temperature was increased directly to the indicated temperatures, not stepwise. In the experiment at 300 °C, the capillary was searched for more intense scattering in the time region marked by two dashed red lines.





Cobalt in ethanol

Here, Co_3O_4 (COD 9005895, $R_f = 9.09$) is formed and transformed into CoO (ICSD 9865, $R_f = 0.951$) with increased reaction temperature and extended time. In the experiment with a reaction temperature of 300 °C, the temperature was increased to 380 °C in steps of 10 °C. In the experiment with a reaction temperature of 250 °C, the temperature was increased in steps of 50 °C.









Cobalt in ethylene glycol

Metallic cobalt is formed at high temperatures while an unknown layered phase is observed at lower temperatures as discussed in the main text. For the experiment at 300 °C, the reactor capillary was scanned for better positions and the temperature was increased to 400 °C; marked with red and white dashed lines. The metallic form primarily crystallizes in an fcc arrangement (ICSD 44989, $R_f = 11.6$), however highly stacking faulted and with nanosized hcp domains (ICSD 44990, $R_f = 38.8$). Both "conventional" Rietveld refinement and PDF refinements (carried out using the xPDFsuite software package) were utilized in order to establish "phase" fractions (84 vol% fcc; 16 vol% hcp) and average hcp domain size (2.4 nm).



Cobalt in Glycerol

L II

10

2θ (°)

1

8

н

6

11 н

12

11.1

14

1.1

Here, cobalt(II) oxide (ICSD 9865, R_f = 1.37) and a minor phase fraction of metallic fcc cobalt (ICSD 44989, R_f = 4.51) forms at 400 °C. Increasing the temperature to 450 °C favor the reduction of cobalt(II), so that the oxide become the minor phase fraction. The metallic phase is heavily stacking faulted and contain almost equal amounts of fcc- and hcp domains when fitting the individual phases.



Co(NO₃)₂ in Glycerol @ 450 °C: Metallic Co (fcc and hcp) + CoO





Iron in 10% hydrogen peroxide solution

After heating to 200 °C, hematite, Fe_2O_3 , (COD 9000139, $R_f = 2.14$) is formed and no further transitions appear with increasing temperature and synthesis time.





Iron in water

Hematite, Fe₂O₃ (COD 9000139, R_f = 4.93), forms at 200 °C.





Iron in ethanol Here, hematite, Fe_2O_3 (COD 9000139, $R_f = 4.93$) also form but at a temperature of 200 °C.



Iron in ethylene glycol

From 300 °C Bragg peaks from magnetite, Fe₃O₄ (COD 9007706, R_f = 1.46) appear and grow. The Rietveld refinements resulted in a good fit; however with an undescribed peak around 3.2 °. This peak is assumed to stem from oxygen vacancy ordering; a well-known phenomenon for Fe₃O₄.²





Iron in glycerol

Magnetite, Fe₃O₄ (COD 9007706, R_f = 2.91) forms at 300 °C. Weak scattering from an unidentified phase is seen between 200 °C and 300 °C.





Manganese in 10% hydrogen peroxide solution

Hausmannite, Mn_3O_4 (ICSD 68174, R_f = 3.20), forms at 300 °C. At 450 °C, the peaks assigned to hausmannite decrease in intensity while new peaks assigned to the manganese silicates, $MnSiO_3$ (COD 1544671, R_f = 5.80) and Mn_2SiO_4 (COD 9015849, R_f = 5.91), appear and grow. The silicate ions are believed to form at high temperature from the fused silica reactor capillary.



Manganese in water

Low intensity Bragg peaks belonging to Mn_2O_3 (COD 1514113, $R_f = 5.57$) appear at 300 °C. These later disappear, presumably because of particle movement in the reaction capillary. When probing other reactor capillary positions, high intensity scattering from Mn_2O_3 is observed.



Manganese in ethanol

Weak scattering from Mn_2O_3 (COD 1514113, $R_f = 17.6$) is observed from 200 °C. At the highest temperature of 450 °C peaks from Mn_3O_4 (ICSD 68174, $R_f = 6.48$) appear. Intense scattering from the phase is observed probing other capillary positions.





Manganese in ethylene glycol

At a temperature of 200 °C, Mn_3O_4 (ICSD 68174, R_f = 10.6) is formed. However, when increasing the temperature to 300 °C, a phase transition to manganese carbonate (COD 1548822, R_f = 3.65) is observed.



Manganese nitrate in Ethylene Glycol: Mn₃O₄



Manganese nitrate in Ethylene Glycol: MnCO₃



Manganese in glycerol

At a temperature of 300 °C MnCO₃ (COD 1548822, $R_f = 3.37$) is formed. When increasing the temperature to 400 °C, peaks indexed to Mn₂SiO₄ (COD 9015849, $R_f = 5.17$) appear and these grow throughout the experiment. The source of silicon must be the reactor capillary made from fused silica. When heating directly to 450 °C, the same pattern is observed: initial formation of MnCO₃ followed by a slow transition to Mn₂SiO₄ ($R_f = 6.66$).









Chromium in 10% hydrogen peroxide solution

Chromium oxyhydroxide, CrOOH, (COD 9012134, $R_f = 1.46$) is formed with a reaction temperature of 400 °C. Increasing the temperature directly to 400 °C in a second experiment yields the same phase phase, but with an improved signal to noise ratio (, $R_f = 1.91$).







Chromium nitrate in hydrogen peroxide: CrOOH



Chromium in water Chromium oxyhydroxide, CrOOH, (COD 9012134, R_f = 3.06) is formed at 400 °C.



Chromium in Ethanol

No Bragg peaks were observed, only very broad features that are insufficient for phase identification. The experiment was repeated with heating directly to 400 °C; this provided the same conclusion.



Chromium in Ethylene glycol

Only a vague signal slowly appears when heating in steps (left), and this was not sufficient for phase identification. When heating directly to 450 °C, Bragg peaks from Cr_2O_3 (COD 9014036, $R_f = 2.50$) slowly grows.









Data Model Difference

20

10

0

20

 $Cr(NO_3)_3$ ·9H₂O in Ethylene Glycol Reaction time [min.] 30

identification. When heating directly to 450 °C, broad Bragg peaks slowly grows. These were however insufficient for unequivocal phase identification.

Heating profile in in situ solvothermal synthesis experiments

The small sample volume (0.85 mm outer diameter of the reaction capillary) and use of a relatively powerful hot air blower results in high heating rates: the targeted temperature is reached within 3-5 seconds. Below is shown the calibration curves from one beamtime.



In most experiments, the temperature was increased in steps from room temperature to 450 °C. Each step temperature, 100 °C, 200 °C, 300 °C, 400 °C, & 450 °C, was held for five minutes before increasing the temperature. This heating scheme has similarities with the lower heating rates of conventional autoclave synthesis, and allow formation of phases stable at low or medium temperatures and intermediates. The heating scheme is illustrated below.



References

- 1. J. Rodriquez-Cavajal, *Physica B*, 1993, **192**, 55-69
- 2. J.-E. Jørgensen, L. Mosegaard, L. E. Thomsen, T. R. Jensen and J. C. Hanson, *J. Solid State Chem.*, 2007, **180**, 180-185.