Electronic Supporting Information (ESI)

Exploring the direct synthesis of exchange-spring nanocomposites by reduction of $CoFe_2O_4$ spinel nanoparticles using *in situ* neutron diffraction

Jakob Voldum Ahlburg,[a] Cecilia Granados-Miralles,[b] Frederik Holm Gjørup,[a] Henrik Lyder Andersen,[a,c] and Mogens Christensen[a]

a. Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, 8000 Aarhus, Denmark

b. Electroceramics Department, Instituto de Cerámica y Vidrio, CSIC, Kelsen 5, ES 28049 Madrid, Spain

c. Current affiliation: School of Chemistry, UNSW Australia, Sydney NSW 2052, Australia

Rietveld refinement of as prepared $CoFe_2O_4$

Here the refined powder X-ray diffraction data obtained using the Rigaku Smartlab equipped with Co-source is shown.

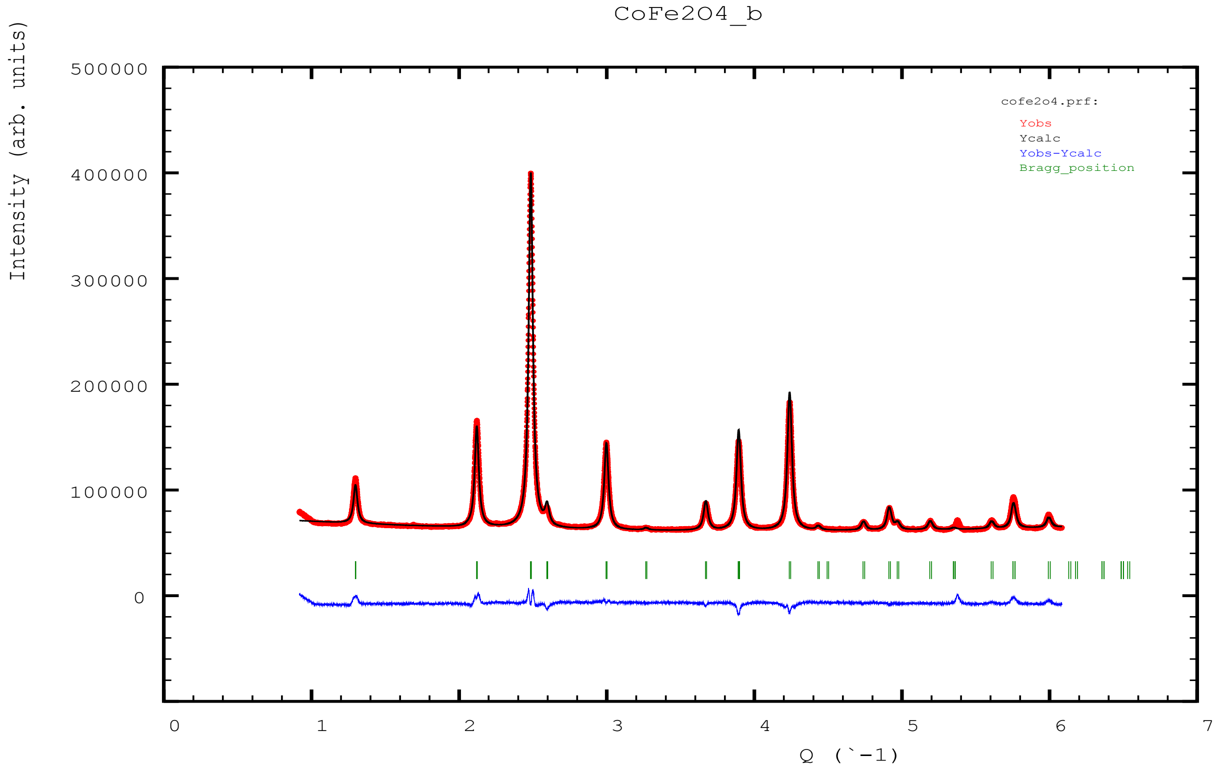

Figure ESI 1: X-ray powder diffraction pattern of as prepared $CoFe_2O_4$.

Results

Time-resolved neutron powder diffraction

The time-resolved neutron powder diffraction data for the experiment not presented in the article can be found here. The experimental parameters are mentioned above the figure.

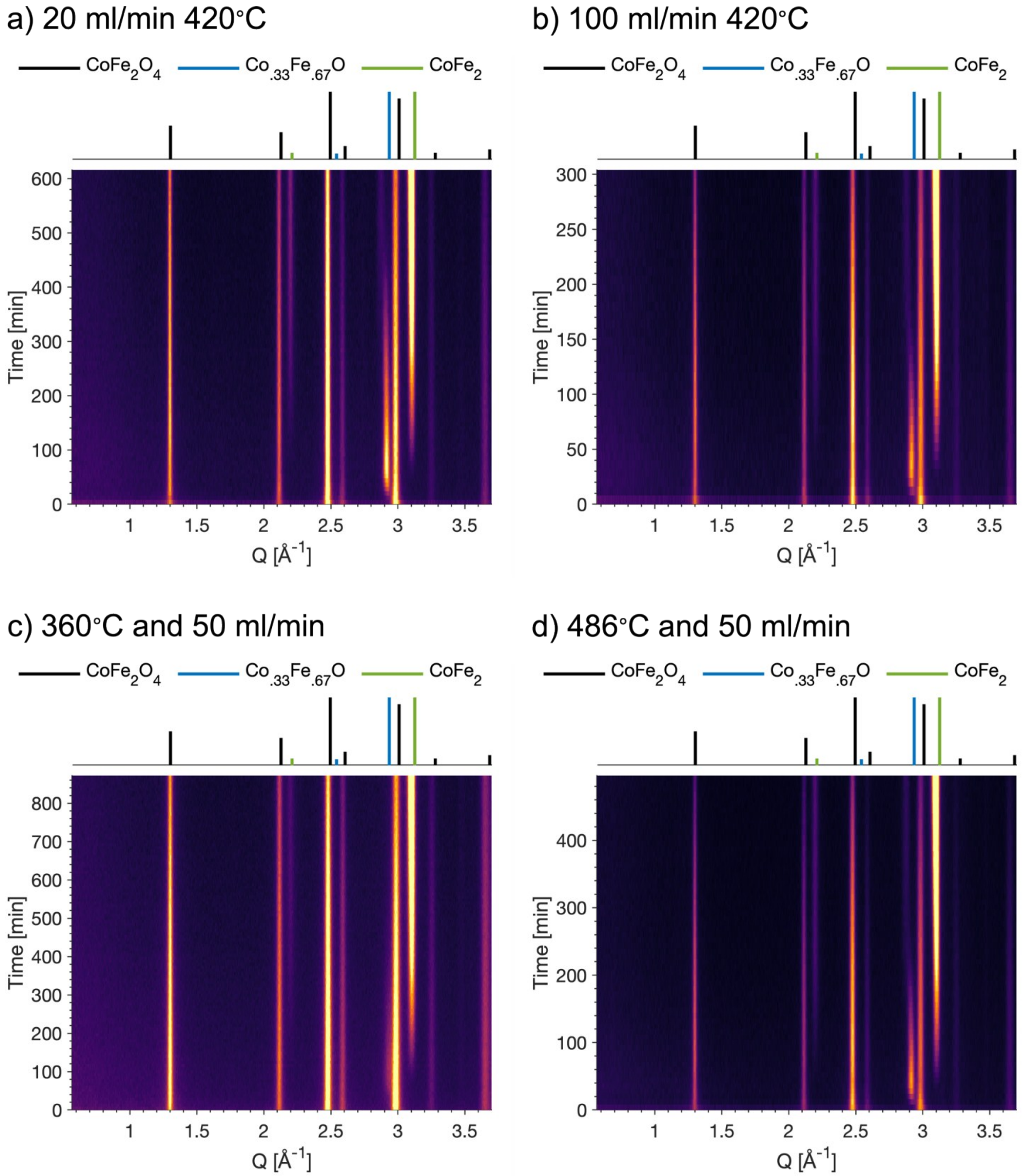

Figure ESI 2: Contour plots of time-resolved NPD obtained for the experiments not presented in the manuscript.. Three phases have been identified and the expected Bragg positions are identified at the top of the figure. Dark colours correspond to low intensities and bright colours to high inte nsities.

R_f-factors

For all refinement, the R_f factor for the $CoFe_2$ phase at the beginning of the experiments is unphysical, as the phase is not yet present. For this reason, the y-limit in some figures has been limited to show only R_f values obtained once a given phase can be clearly identified in the data.

In general, the R_f values for all phases never goes higher than 6.5 % which mean that the phases are well described. The only exception is the $CoFe_2O_4$ phase in the experiment at 542 °C and a flow of 50 ml/min. Here, a very high R_f value up to 18 % is seen late in the experiment. This means that at this point the phase is not as well described which is evident in the uncertainties on the refined parameters presented in the paper.

T = 360 °C flow of 50 ml/min

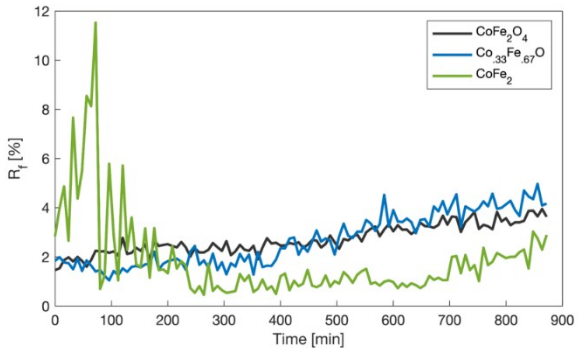

Figure ESI 3: R_f factor for experiment performed at T = 360 ℃ flow of 50 ml/min

T = 420 °C flow of 50 ml/min

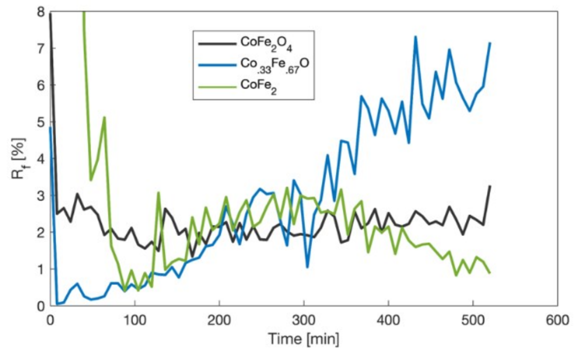

Figure ESI 4: R_f factor for experiment performed at T = 420 ℃ flow of 50 ml/min

T = 486 °C flow of 50 ml/min

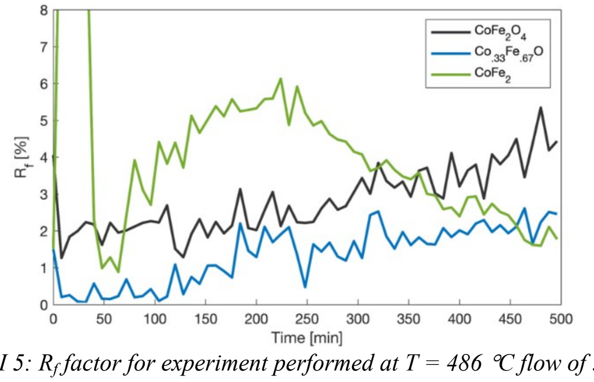

Figure ESI 5: R_f factor for experiment performed at T = 486 ℃ flow of 50 ml/min

T = 542 °C flow of 50 ml/min

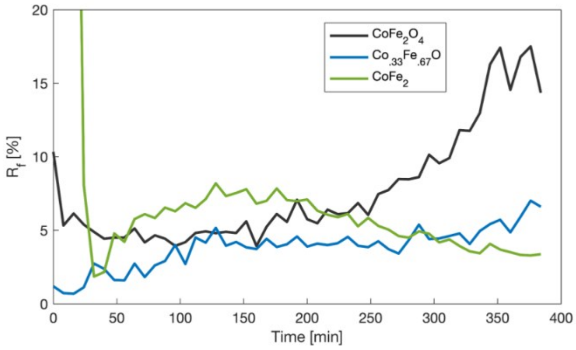

Figure ESI 6: R_f factor for the experiment performed at T = 360 ℃ flow of 50 ml/min

Flow of 20 l/min and a temperature of 486 °C

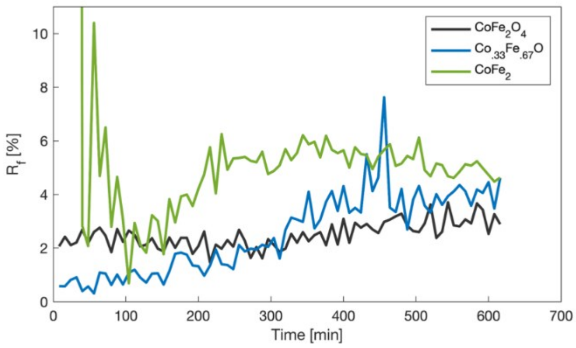

Figure ESI 7: R_f factor for the experiment performed at a flow of 20 ml/min and a temperature of T = 486 ℃.

Flow of 100 l/min and a temperature of 486 °C

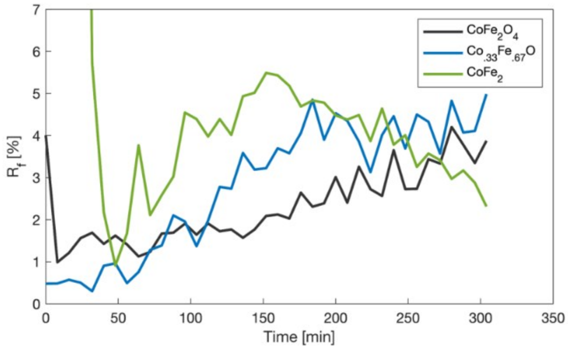

Figure ESI 8: R_f factor for the experiment performed at a flow of 100 ml/min and a temperature of T = 486 ℃.

Refined parameters

Scale factors

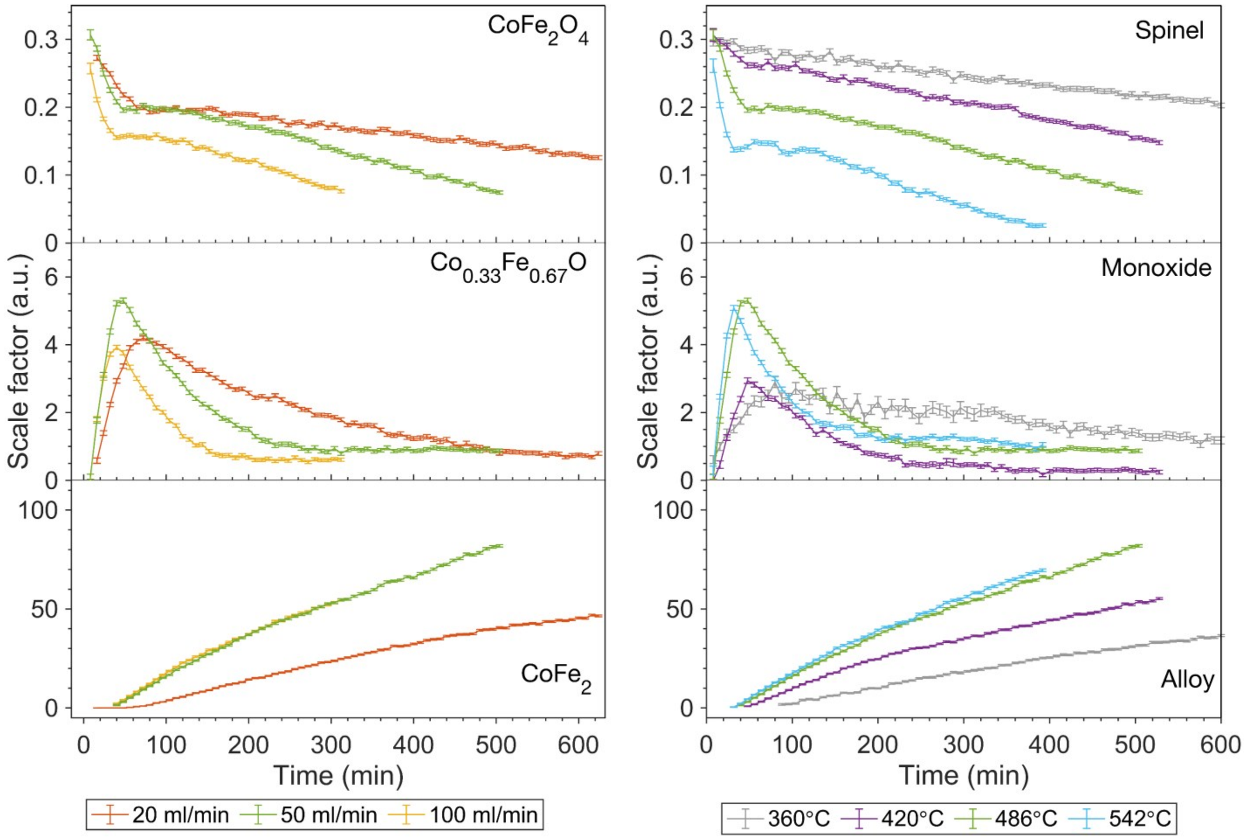

Figure ESI 9:Scale factors obtained from sequential Rietveld refinement as a function of time. ***Left:****The three reduction experiments performed with varying gas-flow of 20 ml/min (red), 50 ml/min (green) and 100 ml/min (yellow) at a temperature of T = 486 ℃.* ***Right:*** *The four reduction experiments performed with varying temperatures of 360 ℃ (plotted on the top grey axis), 420 ℃ (purple), 486 ℃ (green), and 542 ℃ (light blue) and with a gas-flow of 50 ml/min.Uncertainties are obtained from the refinement.*

Refined magnetic moments obtained from GEM@ISIS

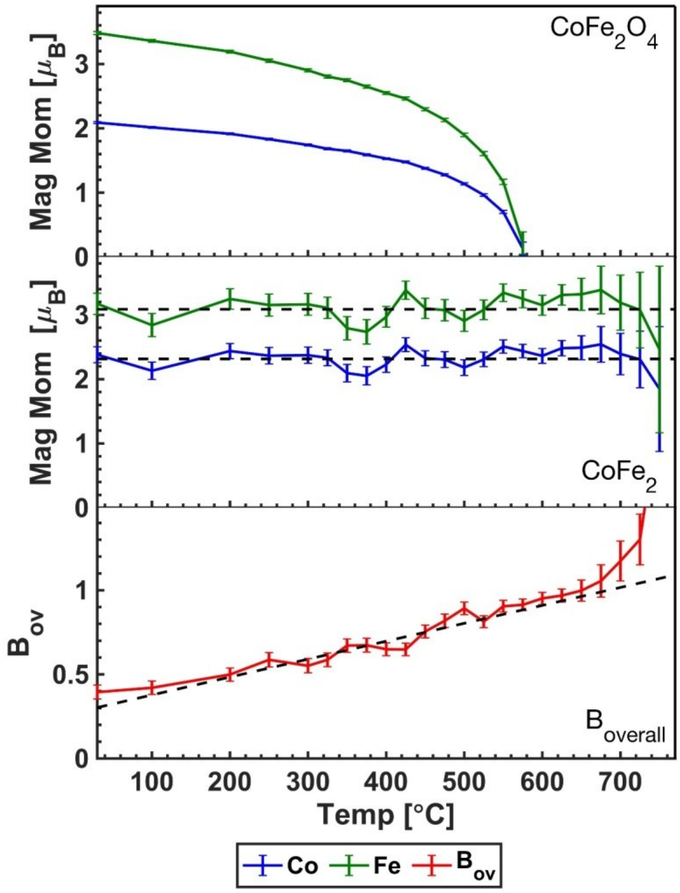

Figure ESI 10: Rietveld refined parameters from data acquired at GEM of the sample produced at 420 °C and 50 ml/min of gas flow. Top: The magnetic moments of Co and Fe in the $CoFe_2O_4$ structure. Middle: The magnetic moments of Co and Fe in the $CoFe_2$ alloy. The dotted lines are the average magnetic moment. Bottom: Overall thermal parameter $B_{overall}$ refined for all phases. The dotted line is a linear fit of the data from T = 30 °C to T = 575 °C. Uncertainties are obtained from the refinement.

The sample reduced at 420 °C and with a gas-flow of V = 50 ml/min was measured using neutron powder diffraction as a function of temperature on the Time-of-Flight neutron diffractometer GEM at ISIS. A 6 mm vanadium sample can was used to contain the sample and the experiment was carried out in vacuum.

The data was sequentially Rietveld refined to obtain the magnetic moments the Co and Fe in the $CoFe_2O_4$ and $CoFe_2$ and the overall thermal parameter B_{ov}. These parameters have been used in the sequential refinement of the *in situ* neutron powder diffraction reduction experiments performed at DMC and described in the article. The magnetic moments obtained for the $CoFe_2O_4$ have been used directly in the refinements. Since the magnetic moment of the $CoFe_2$ slightly fluctuates as a function of temperature, an average magnetic moment was calculated for both Co and Fe and used for refinements at all temperatures. The values are m_{Co} = 2.135 μ_B and m_{Fe}= 3.087 μ_B The refined overall thermal parameters were fitted with a linear function in the temperature range = 0 - 575°C. The function $B_{ov} = 0.0010234 * Temp + 0.3027$ was used to calculate the B_{ov} for all experiments. The same B_{ov} was chosen for all phases.

It is worth mentioning that the refinement of the magnetic moments of the $CoFe_2O_4$ structure furthermore reveals the Curie temperature to be T_C = 575 °C.

Simulated NPD pattern for $CoFe_2O_4$, γ–Fe_2O_3, and Fe_3O_4

The Simulated data seen in Figure ESI 11 shows a clear distinction between the peak intensities for the isostructural $CoFe_2O_4$, γ–Fe_2O_3, and Fe_3O_4. Since the intensities are proportional to the site occupancy of the tetragonal (Td) and octahedral (Oh) site, it is possible to distinguish the three phases by varying the site occupancies. The unit cell parameters used for the simulations were 8.39 Å, 8.33 Å, and 8.40 Å for $CoFe_2O_4$, γ–Fe_2O_3, and Fe_3O_4, respectively The model was based on the same volume of sample with a magnetic moment for iron $m_{Fe} = 3.1\ \mu_B$ and for cobalt $m_{Co} = 2.1\ \mu_B$. The particle modelled particle size was 25 nm.

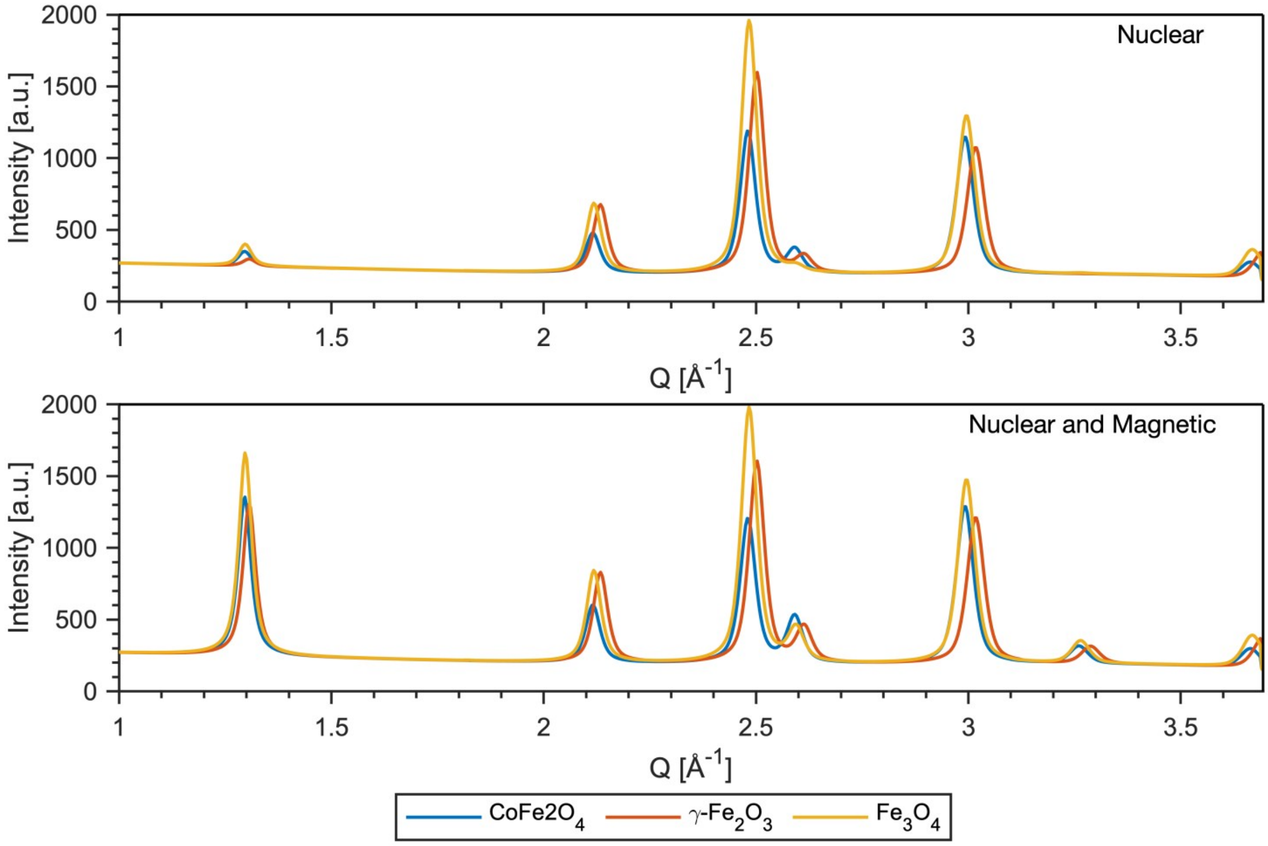

Figure ESI 11: Simulated NPD patterns for $CoFe_2O_4$, γ–Fe_2O_3, and Fe_3O_4. Top: only the structure has been simulated with no magnetic contribution. Bottom: Both the nuclear and a magnetic structure is simulated.

Sequential Rietveld refinement

The crystallographic description of the phases in the Rietveld refinement is described below. Two models are described for the $CoFe_2O_4$: One for the Pristine $CoFe_2O_4$, where the final values from the refinements are presented and another used during the sequential refinement.

Ions	Wyckoff position	Atomic position			Site Occupancy [%]	Site Occupancy Refined
		x	y	z		
O^{2-}	32e	0.258	0.258	0.258	100%	0.16667
Co^{2+} (Td)	8b	3/8	3/8	3/8	28.9%	0.01205
Fe^{3+} (Td)	8*b*	3/8	3/8	3/8	71.1%	0.02962
Co^{2+} (Oh)	16*c*	0	0	0	35.6%	0.02964
Fe^{3+} (Oh)	16*c*	0	0	0	64.4%	0.05370

Table ESI 1: Crystallographic description of the pristine $CoFe_2O_4$ (spinel). Space group Fd-3m (#227), with a total multiplicity of 192.

Ions	Wyckoff position	Atomic position			Site Occupancy [%]	Site Occupancy Refined
		x	y	z		
O^{2-}	32e	x_O	x_O	x_O	100%	0.16667
Co^{2+} (Td)	8b	3/8	3/8	3/8	$occ\%_{Co}^{Td}$	occ_{Co}^{Td}
Fe^{3+} (Td)	8*b*	3/8	3/8	3/8	100% - $occ\%_{Co}^{Td}$	0.04167 - occ_{Co}^{Td}
Co^{2+} (Oh)	16*c*	0	0	0	$occ\%_{Co}^{Oh}$	occ_{Co}^{Oh}
Fe^{3+} (Oh)	16*c*	0	0	0	100% - $occ\%_{Co}^{Td}$	0.08334 - occ_{Co}^{Oh}

Table ESI 2: Crystallographic description of the $CoFe_2O_4$ (spinel) during sequential refinement. Space group Fd-3m (#227), with a total multiplicity of 192. x and occ are refined values.

Ions	Wyckoff position	Atomic position			Site Occupancy [%]	Site Occupancy Refined
		x	y	z		
O^{2-}	4b	0.5	0.5	0.5	100%	0.02083
Co^{2+}	4a	0	0	0	33.3%	0.00694
Fe^{2+}	4a	0	0	0	66.7%	0.01389

Table ESI 3 Crystallographic description of the $Co_{0.33}Fe_{0.67}O$ (monoxide) for all samples and refinements. Space group Fm-3m (#225), with a total multiplicity of 192.

Ions	Wyckoff position	Atomic position			Site Occupancy [%]	Site Occupancy Refined
		x	y	z		
Fe^0 (*Me*1)	1a	0	0	0	100%	0.02083
Co^0 (*Me*2)	1b	0.5	0.5	0.5	66.7%	0.00694
Fe^0 (*Me*2)	1b	0.5	0.5	0.5	33.3%	0.01389

Table ESI 4: Crystallographic description of the $CoFe_2$ (alloy) for all samples and refinements. Space group Pm-3m (#221), with a total multiplicity of 48.

Magnetic hysteresis data

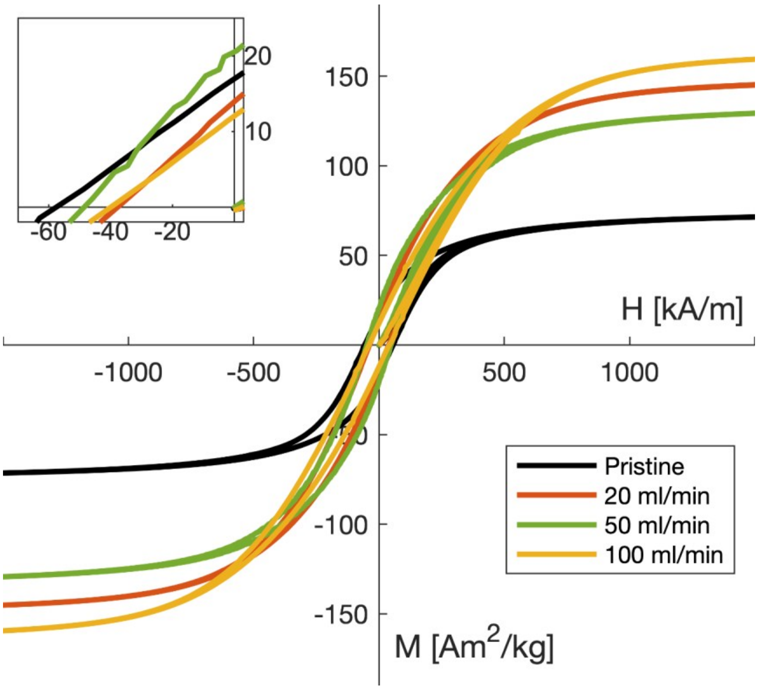

Figure ESI 12: Magnetic hysteresis data acquired using a PPMS with the VSM option. The samples presented are the pristine $CoFe_2O_4$ (black) and the samples reduced with a gas-flow of $\dot{V}$ = 20 ml/min (orange), 50 ml/min (green), 100 ml/min (yellow) with a temperature of T = 486 ℃. The inset is a zoom of the 2nd quadrant.

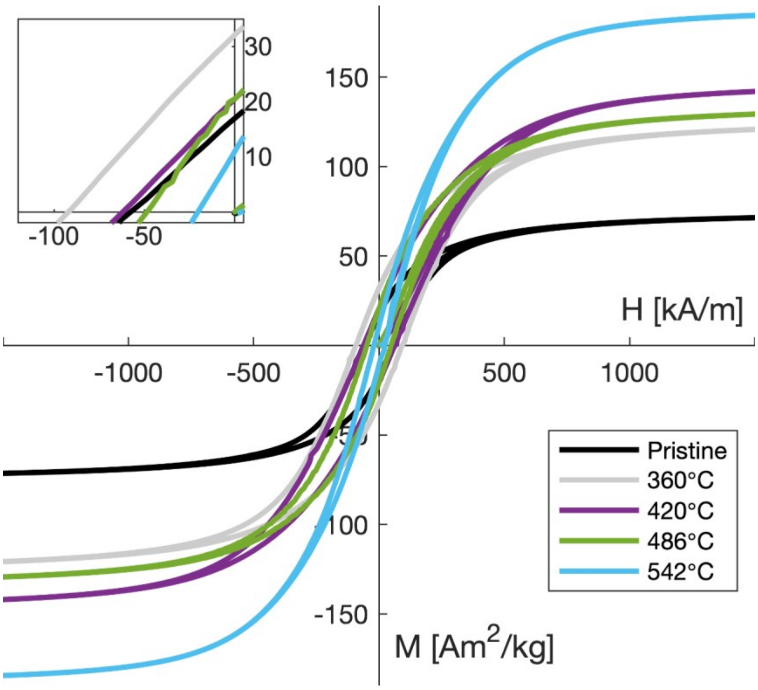

Figure ESI 13: Magnetic hysteresis data acquired using a PPMS with the VSM option. The sample presented are the pristine $CoFe_2O_4$ (black) and the sample reduced at T = 360 ℃ (grey) , T = 420℃ (purple), T = 486 ℃ (green) and T = 542 ℃ (light blue) with a gas flow of $\dot{V}$ = 50 ml/min. The inset is a zoom of the 2nd quadrant.

Sample Composition, particle size and Magnetic properties of reduced samples

Sample Id	Spinel		MeO	Alloy		Magnetic properties		
	wt.%	**<D>** nm	**wt.%**	**wt.%**	**<D>** nm	**σ_s** Am^2/kg	**σ_r** Am^2/kg	**H_c** kA/m
"Pristine"	**100**	*13.2(3)*	**0**	**0**	-	73.9(1)	16.9(1)	56(1)
"360"	**56(1)**	*27.5(4)*	**6.1(6)**	**38.2(7)**	*35.6(6)*	125.0(4)	32.0(2)	93(1)
"420"	**52(1)**	*33.6(4)*	**1.6(4)**	**46.8(7)**	*43.5(6)*	146.7(2)	20.3(2)	62.7(9)
"486", "50mlmin"	**25.5(8)**	*43(1)*	**6.0(4)**	**68.5(9)**	*43.5(5)*	133.1(2)	20.5(4)	48.2(9)
"542"	**12(1)**	*78(8)*	**9.7(6)**	**78(1)**	*52.2(8)*	188.4(2)	10.8(4)	20.0(7)
"20mlmin"	**49(1)**	*50(1)*	**6.2(4)**	**44.4(7)**	*60.3(1)*	149.1(4)	13.8(2)	37.8(8)
"100mlmin"	**34(1)**	*52.9(9)*	**5.5(4)**	**60(1)**	*45.5(7)*	165.0(4)	12.0(2)	39.6(7)

ES 1: The weight fraction [wt%], crystallite size [<D>], saturation magnetisation[σ_s], remanence [σ_r] and coercivity [H_C] for the $CoFe_2O_4$ spinel, the $Co_{0.33}Fe_{0.67}O$ monoxide (MeO) and the $CoFe_2$ alloy. The samples presented are: the pristine $CoFe_2O_4$, the samples prepared at T = 360, 420, 486, and 542 ℃ with a gas flow of V = 50 ml/min, and the samples prepared at a gas-flow of V = 20 and 100 ml/min at a temperature of T = 486 ℃. Uncertainties on weight-fraction and crystallite size are obtained from the Rietveld refinement. Uncertainties on magnetic properties are obtained from the data treatment to obtain the values.