Supporting information

Very fast crystallisation of MFe_2O_4 spinel ferrites (M=Co, Mn, Ni, Zn) under low temperature hydrothermal conditions: a time-resolved structural investigation

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Table S1 *Targeted compound and corresponding synthesis details*

Sample	**Target Compound**	**Treatment Time/hours**	**Yield %**	**Confirmed by XRD**
I-Co060-1	$CoFe_2O_4$	1	62	yes
I-Co060-3	$CoFe_2O_4$	3	73	yes
I-Co060-6	$CoFe_2O_4$	6	78	yes
I-Co060-9	$CoFe_2O_4$	9	50	yes
I-Co060-12	$CoFe_2O_4$	12	85	yes
I-Co060-18	$CoFe_2O_4$	18	80	yes
I-Co060-24	$CoFe_2O_4$	24	87	yes
I-Mn060-1	$MnFe_2O_4$	1	90	yes
I-Mn060-3	$MnFe_2O_4$	3	79	yes
I-Mn060-6	$MnFe_2O_4$	6	88	yes
I-Mn060-9	$MnFe_2O_4$	9	83	yes
I-Mn060-12	$MnFe_2O_4$	12	91	yes
I-Mn060-18	$MnFe_2O_4$	18	87	yes
I-Mn060-24	$MnFe_2O_4$	24	96	yes
I-Ni060-1	$NiFe_2O_4$	1	96	Presence of spurious phases
I-Ni060-3	$NiFe_2O_4$	3	88	Presence of spurious phases
I-Ni060-6	$NiFe_2O_4$	6	88	yes
I-Ni060-9	$NiFe_2O_4$	9	93	yes
I-Ni060-12	$NiFe_2O_4$	12	91	yes

I-Ni060-18	$NiFe_2O_4$	18	88	yes
I-Ni060-24	$NiFe_2O_4$	24	89	yes
I-Zn060-1	$ZnFe_2O_4$	1	75	yes
I-Zn060-3	$ZnFe_2O_4$	3	74	yes
I-Zn060-6	$ZnFe_2O_4$	6	67	yes
I-Zn060-9	$ZnFe_2O_4$	9	68	yes
I-Zn060-12	$ZnFe_2O_4$	12	71	yes
I-Zn060-18	$ZnFe_2O_4$	18	78	yes
I-Zn060-24	$ZnFe_2O_4$	24	84	yes

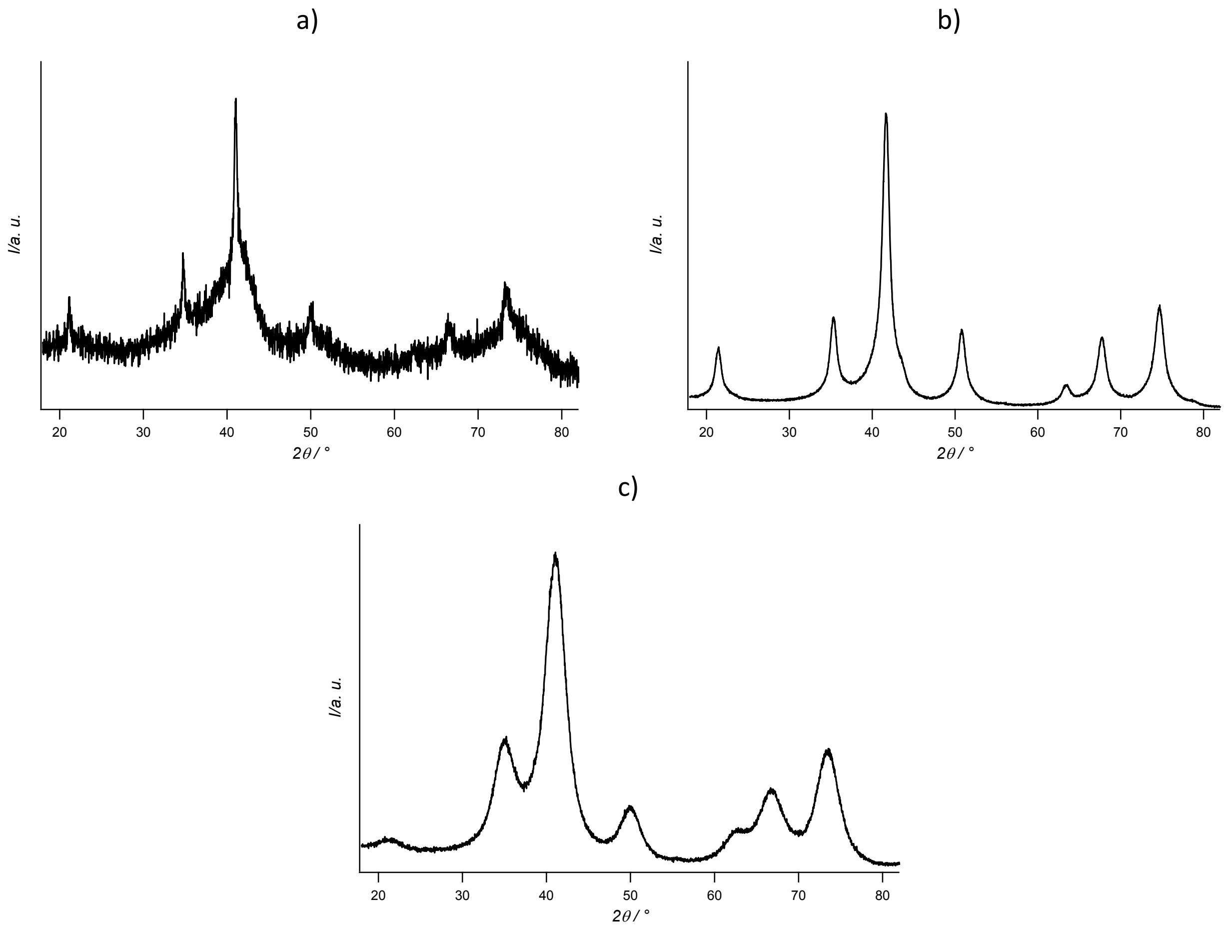


Figure S1 *XRD diffractograms registered after 30 min of hydrothermal treatment for a) Mn, b) Co and c) Zn ferrite*

In order to study the interaction of oxalic acid with the transition metal salts during the co-precipitation phase, the reaction was stopped after the basification step. The formed solid phase was isolated through centrifugation and FTIR spectra were collected; the solid was then once more suspended in deionised water and centrifuged twice, washing each time with deionised water to eliminate any sodium oxalate which may be part of the precipitate (sodium oxalate has a solubility of 36.1 g/l in water [1]). Barium sulphate in a 1:1 molar ratio to the oxalic acid was added to the precipitate from the suspensions, to act as an insoluble reference to better visualize possible decrease in intensity of signals related to soluble products. The collected spectra (**Figure S2**) mainly feature the peaks typical of barium sulphate (in particular the three bands at 1190, 1120 and 1070 cm^{-1}), but in the spectra collected before washing a small band is visible at around 1620 cm^{-1}, and is typical of oxalates. This band disappears with washing. Given its disappearance, it can thus be concluded that only the metal hydroxides precipitate during the preliminary synthesis phase, with a small amount of sodium oxalate forming alongside them. This is in agreement with the lower solubility of the transition metal hydroxides involved compared to the relative oxalates as well as the high OH^- concentration in the system (see **Table S2**). It should however be noted that these results only refer to the solid material precipitated at room temperature and pressure, and they do not preclude the participation of the oxalate group to the reaction once the system has been brought to 135°C and subjected to the autogenous pressure from the acid digestion bomb closed reactor.

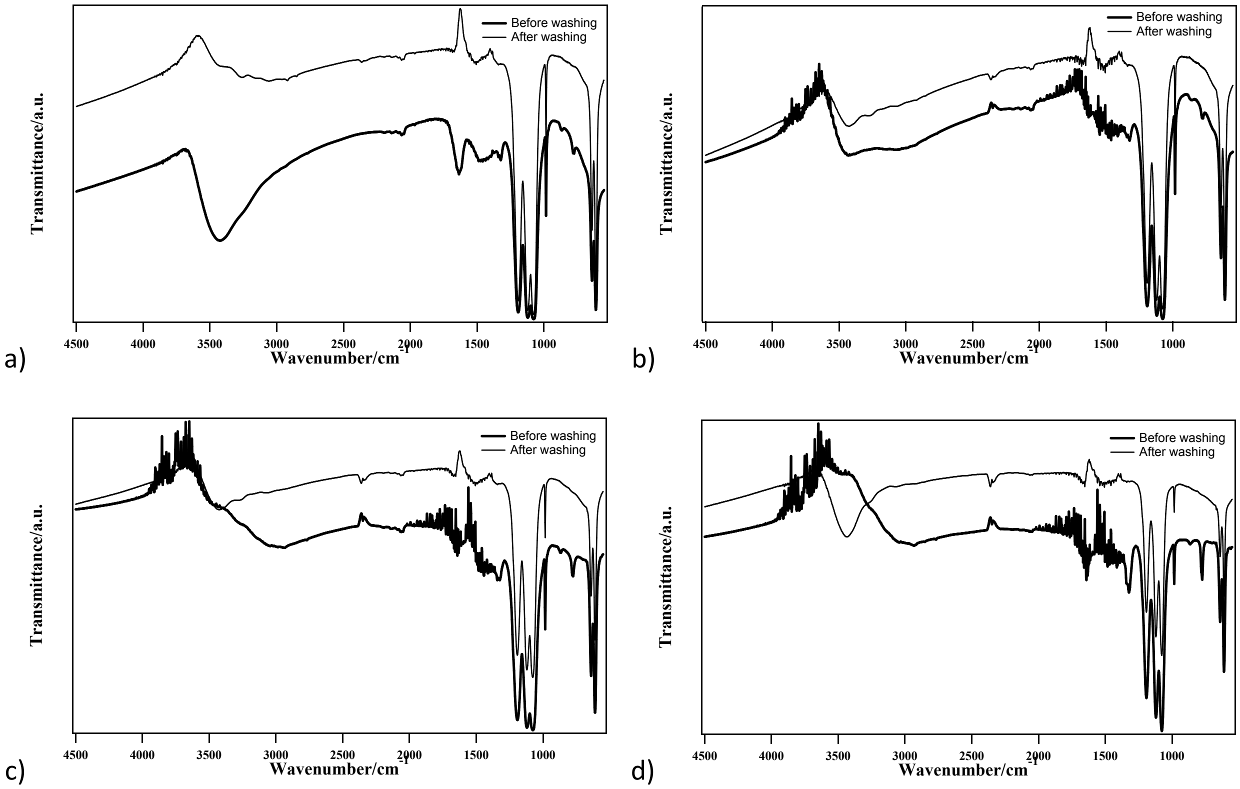


Figure S2 *Transmission FTIR spectra of the precipitated precursors (after adding NaOH and* $BaSO_4$*) for a)* $CoFe_2O_4$*, b)* $MnFe_2O_4$*, c)* $NiFe_2O_4$ *and d)* $ZnFe_2O_4$*,*

Table S2 *Solubility of the M-metal hydroxide and oxalate salts in water at 20°C*[1]

Transition metal	Solubility of the hydroxide in water (g/100 ml)	Solubility of the oxalate in water (g/100 ml)
Cobalt	$3.2*10^{-4}$	$3.7*10^{-3}$
Manganese	$3.4*10^{-4}$	$2.8*10^{-2}$

Nickel	$1.5*10^{-4}$	$1.2*10^{-3}$
Zinc	$4.2*10^{-5}$	$2.6*10^{-3}$

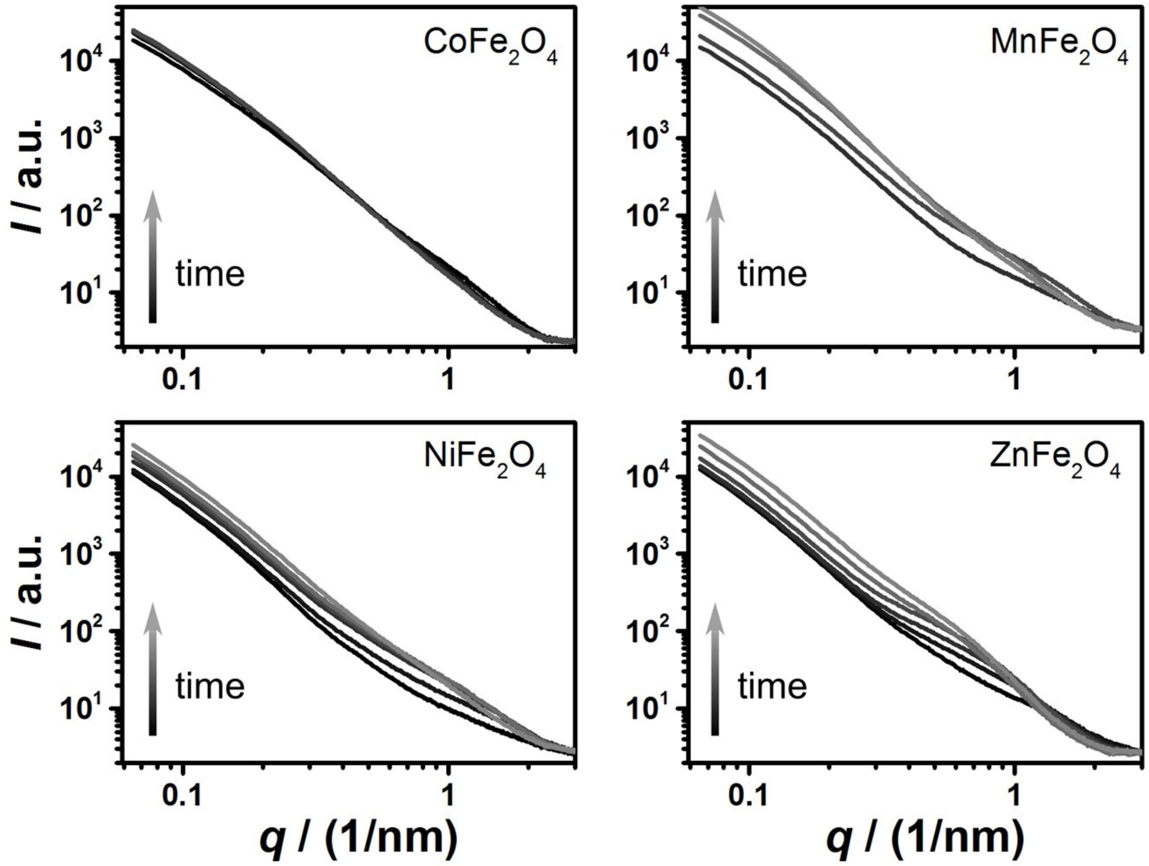


Figure S3 *In-situ SAXS data for the different ferrite particle syntheses.*

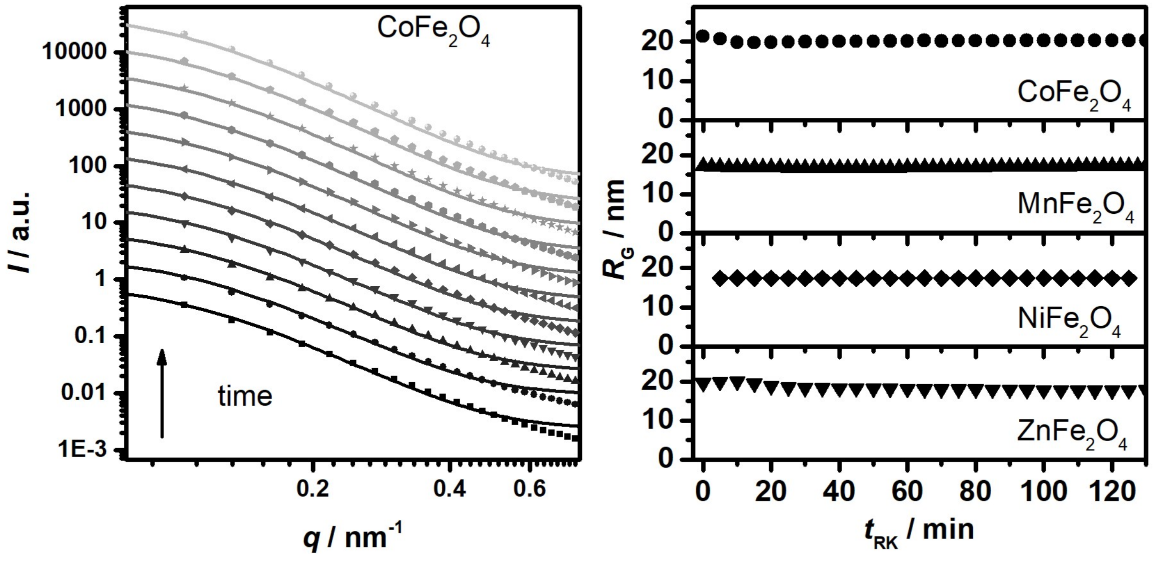


Figure S4 *Evolution of the radius of Gyration according to the Beaucage model (see Experimental Section), applied to in-situ SAXS data. Left: $CoFe_2O_4$ in-Situ measurements comparison of data points(reduced for clarity by a factor of 6) and fitted curves of Beaucage model. Right: Development of Gyration radii over time.*

In-situ SAXS data were taken every 5 min, up to a reaction time of 120 min. The *in situ* SAXS data reveal only small differences in the course of the heat treatment for all ferrites under investigation. In contrast to the ex-situ SAXS data, the in-situ SAXS data allowed for a quantitative analysis. While a form factor analysis was not possible because of the lack of pronounced minima, the SAXS data corresponded to a diluted system and could thus be fitted at small scattering angles, in order to determine the radius of gyration. The Beaucage approach was successfully applied to fit the in-situ SAXS data and provided, as major parameter, the Guinier radius. R_g derived from the SAXS data using the Beaucage approach (Experimental Part) were almost constant over time, which was already indicated by the SAXS data themselves. For all ferrites under study a radius of gyration of ca. 20 nm was determined, while it should be noted that the experimental range of q and also the Beaucage approach do not allow for the detection and quantification of small particles (diameter below ca. 5 nm).

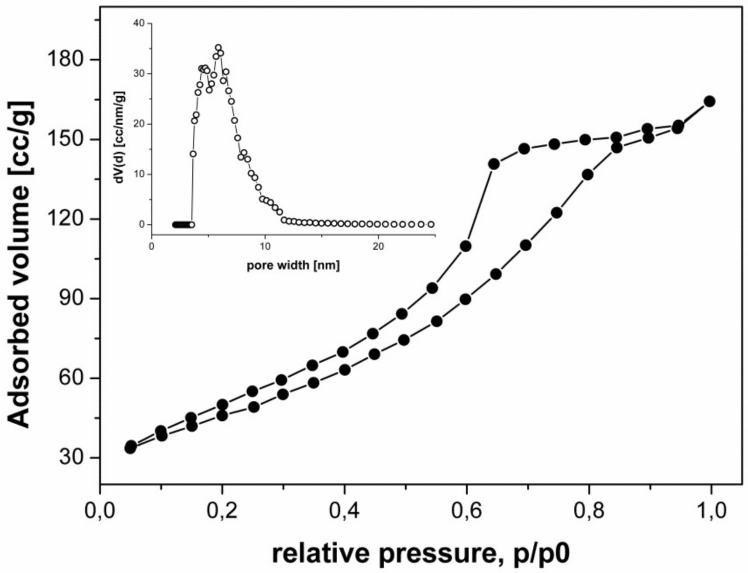
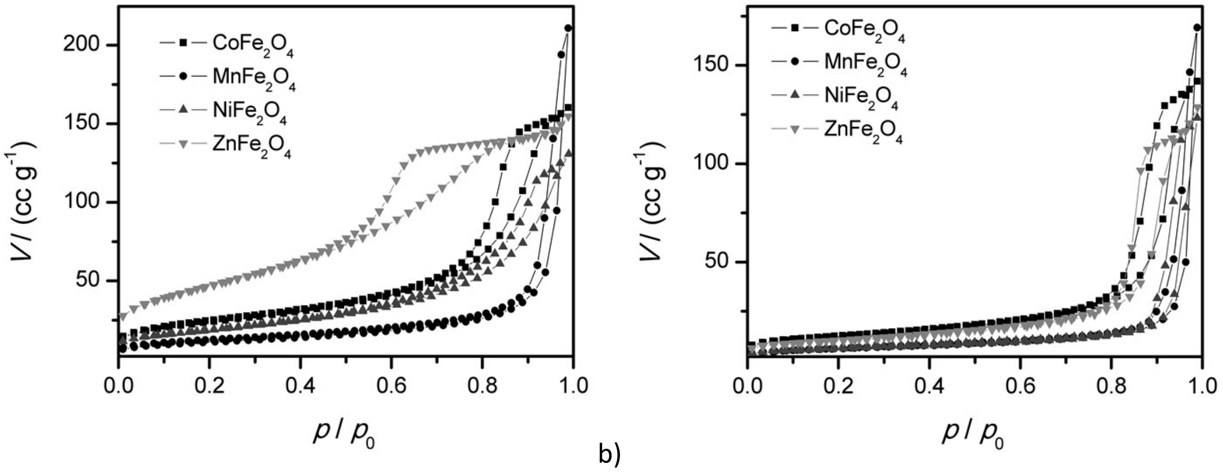


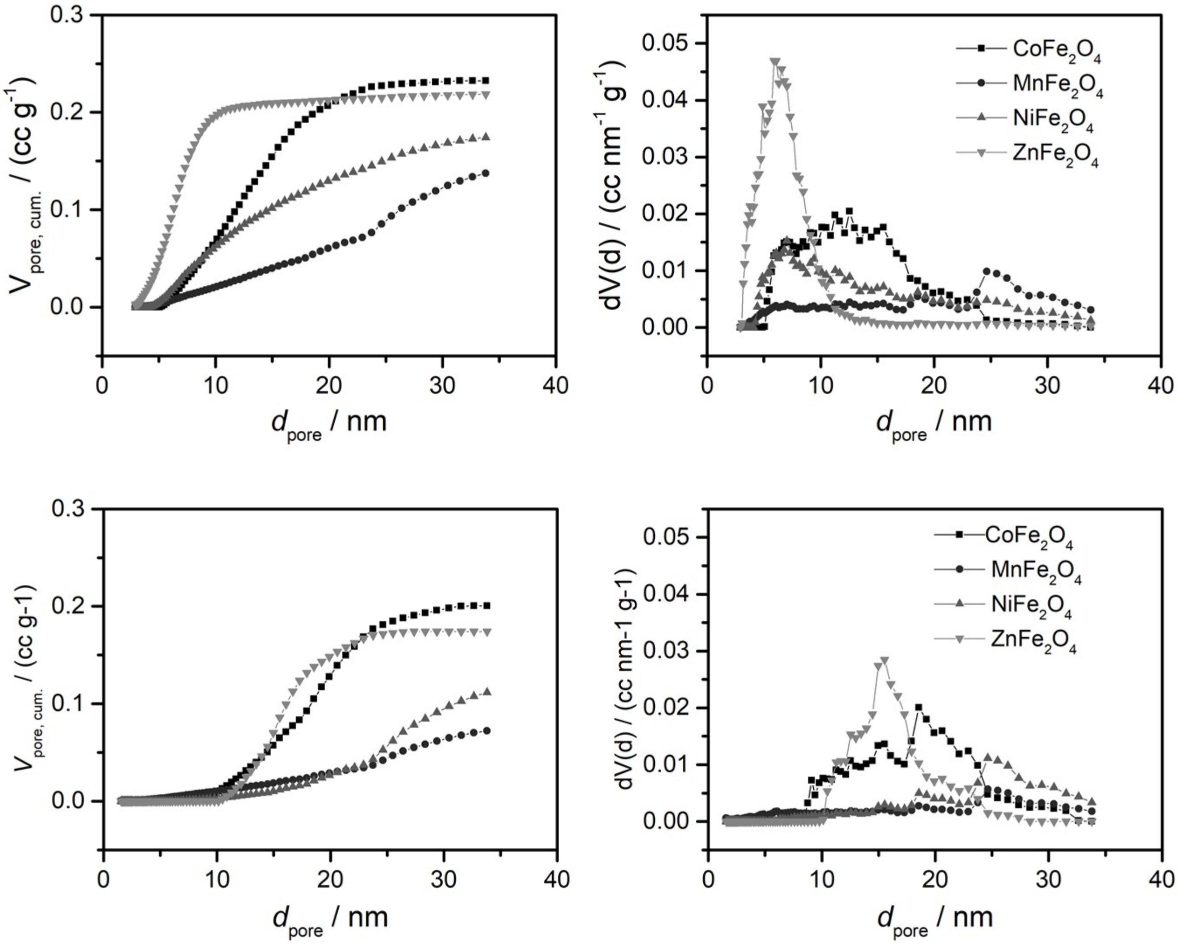
Figure S5 *Nitrogen physisorption isotherm of the zinc ferrite together with the NLDFT pore size distribution plot (left-side inset).*

The porosity of the ferrites was investigated by means of nitrogen physisorption experiments. Manganese, cobalt and nickel materials show a type II isotherm (**Figure S6**), typical of non-porous or macroporous solids[2], with specific surface areas as high as 77 m^2/g (**Table S3**).



a) b)

Figure S6 *Nitrogen physisorption isotherms of the investigated ferrites a) as synthesized and b) after calcination in air at 600°C for 3 hours.*



a)

b)

Figure S7 *Pore size distributions (left: cumulative; right: differential) of the investigated ferrites a) as synthesized and b) after calcination in air at 600°C for 3 hours.*

Table S3 *Specific surface area (S_{BET}) and total pore volume (V_P) of the investigated ferrites.*

Sample	**S_{BET} fresh[m^2/g]**	**V_P fresh[cc/g]**	**S_{BET} calc.[m^2/g]**	**V_P calc.[cc/g]**
$NiFe_2O_4$ 24h	75	-	21	

$MnFe_2O_4$ 24h	38	-	21	
$ZnFe_2O_4$ 24h	168	0.24	36	0.20
$CoFe_2O_4$ 24h	77	-	44	

[1] W. M. Haynes, Ed. , *CRC Handbook of Chemistry and Physics, 93rd Edition*, Taylor & Francis, Boca Raton, **2012**.

[2] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure Appl. Chem.* **2015**, *87*, DOI 10.1515/pac-2014-1117.