Electronic Supplementary Material (ESI) for CrystEngComm

SUPPORTING INFORMATION

Direct Synthesis and Mechanism of the Formation of Mixed Metal Fe_2Ni-MIL-88B

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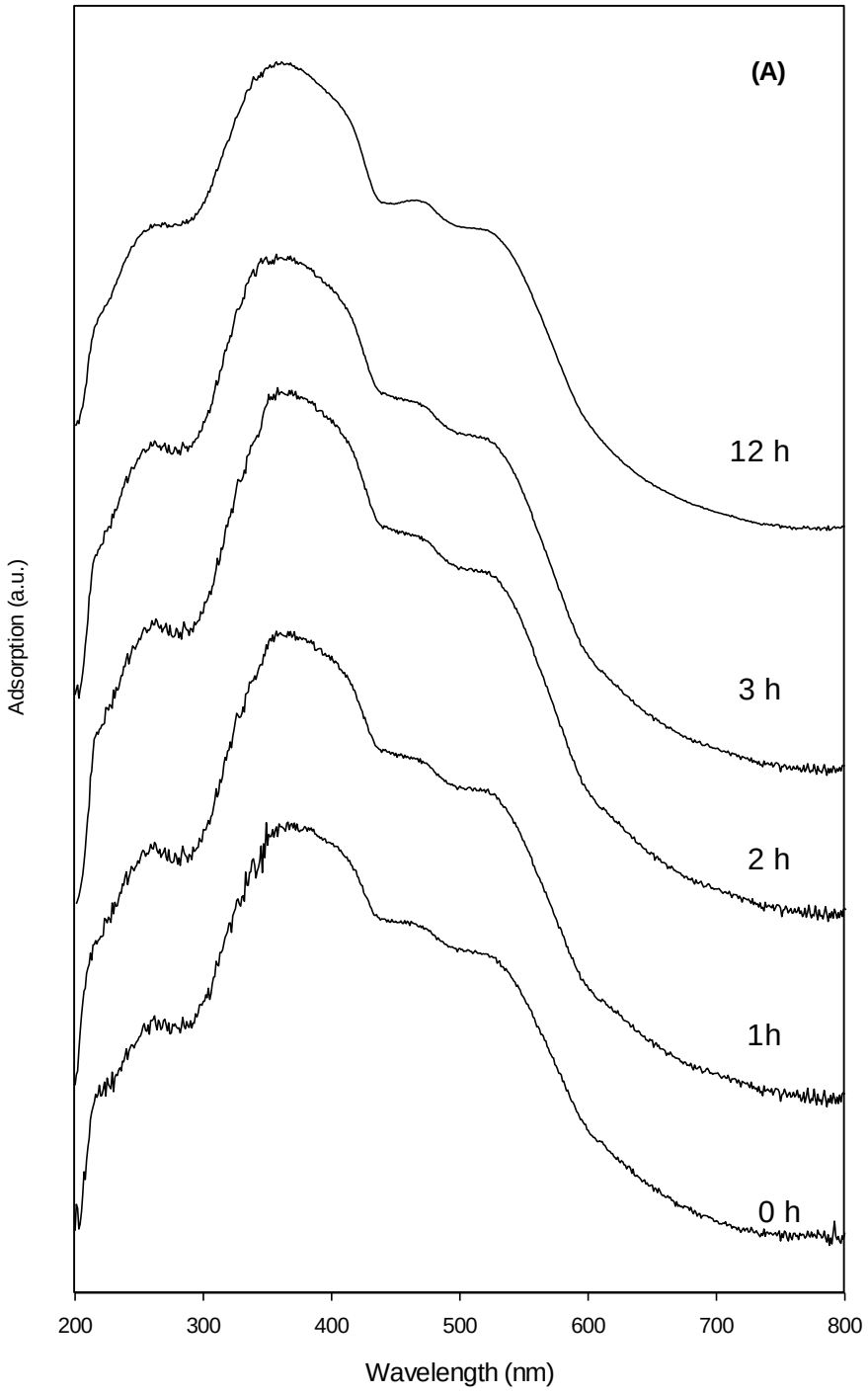
1. UV-Vis spectra



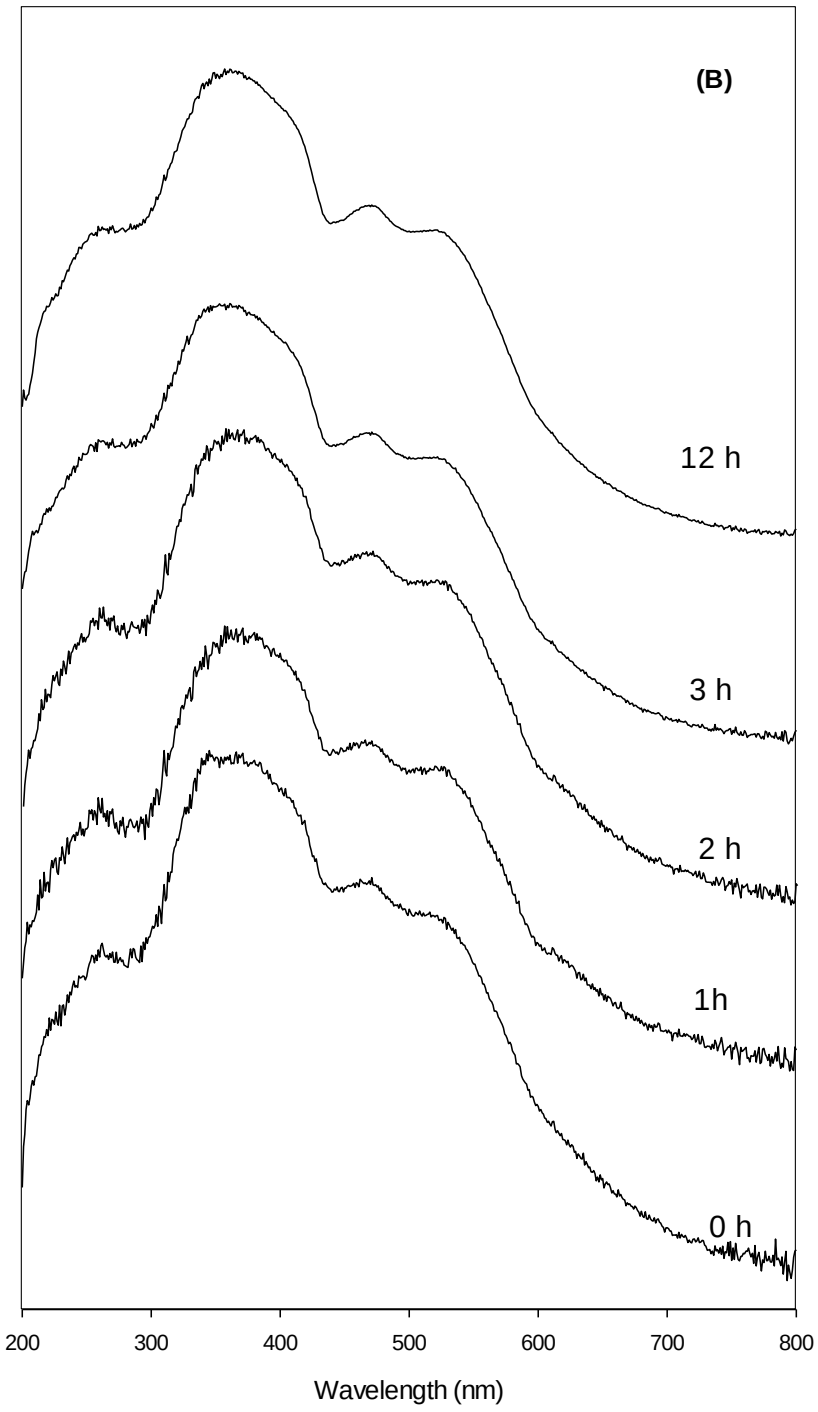
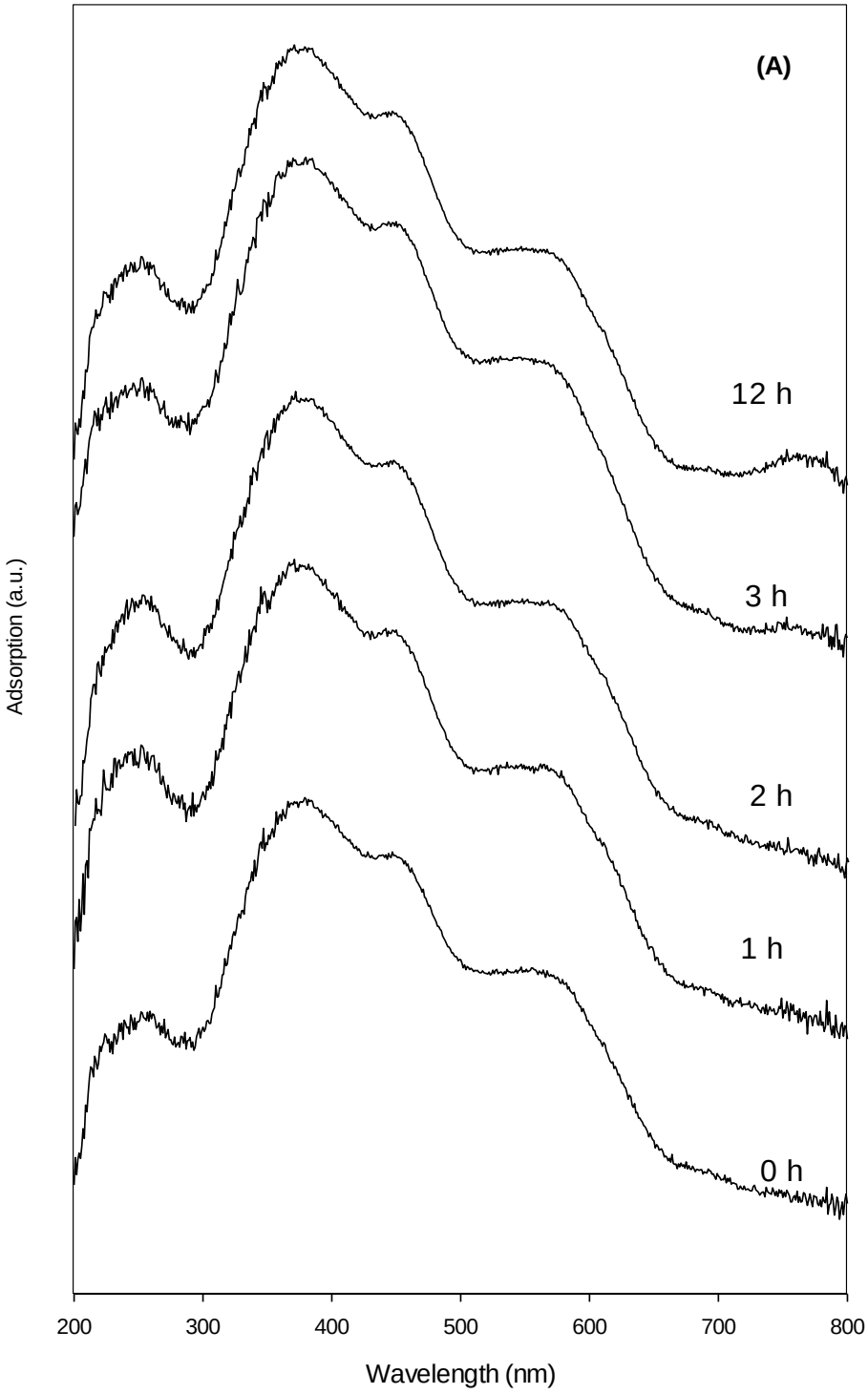


Fig. S1 UV-Vis spectra of the samples Fe_3-NO_3-x (A) and Fe_3-Cl-x (B) prepared using $Fe(NO_3)_3.9H_2O$ and $FeCl_3.6H_2O$, respectively, at different synthesis times.



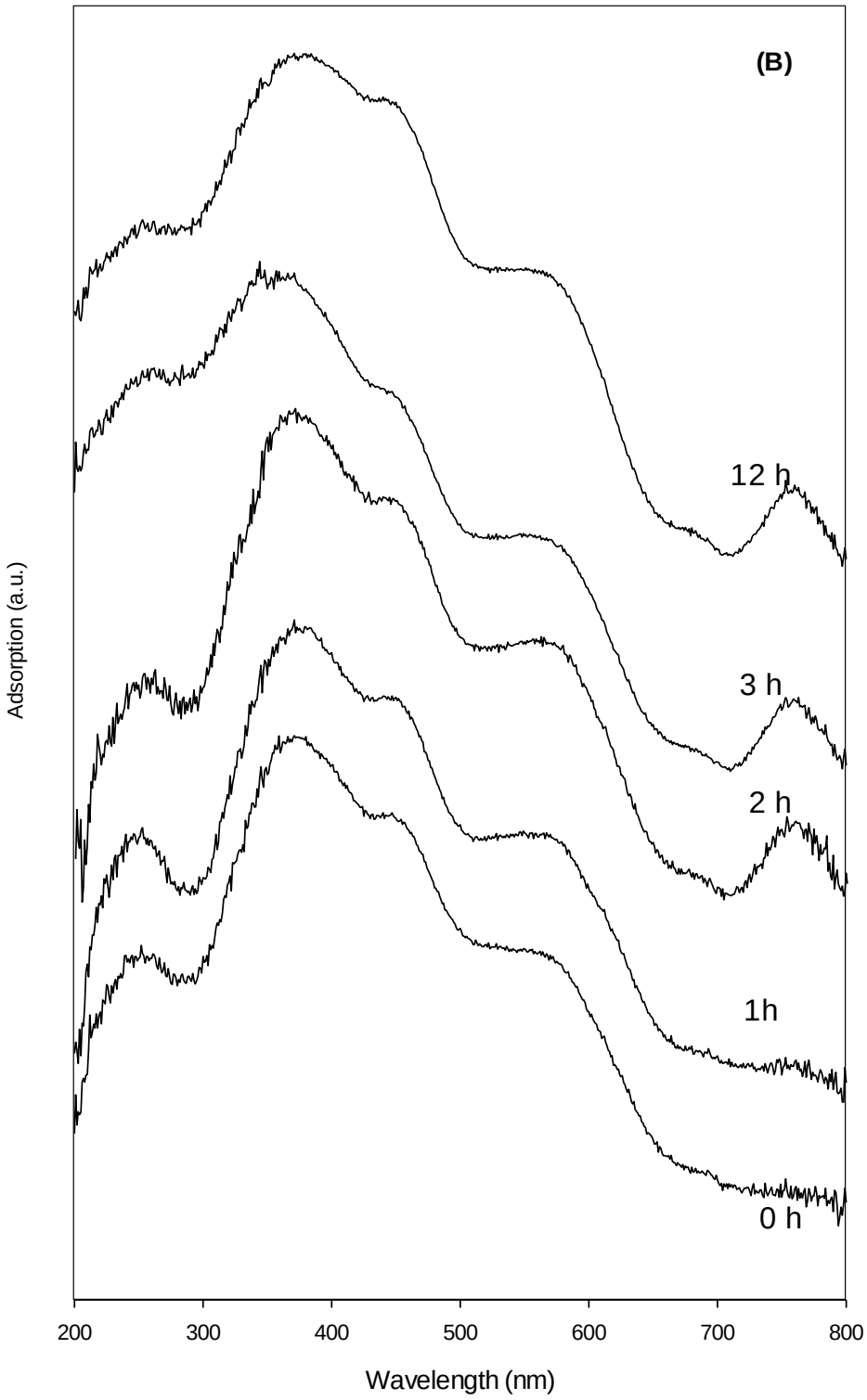
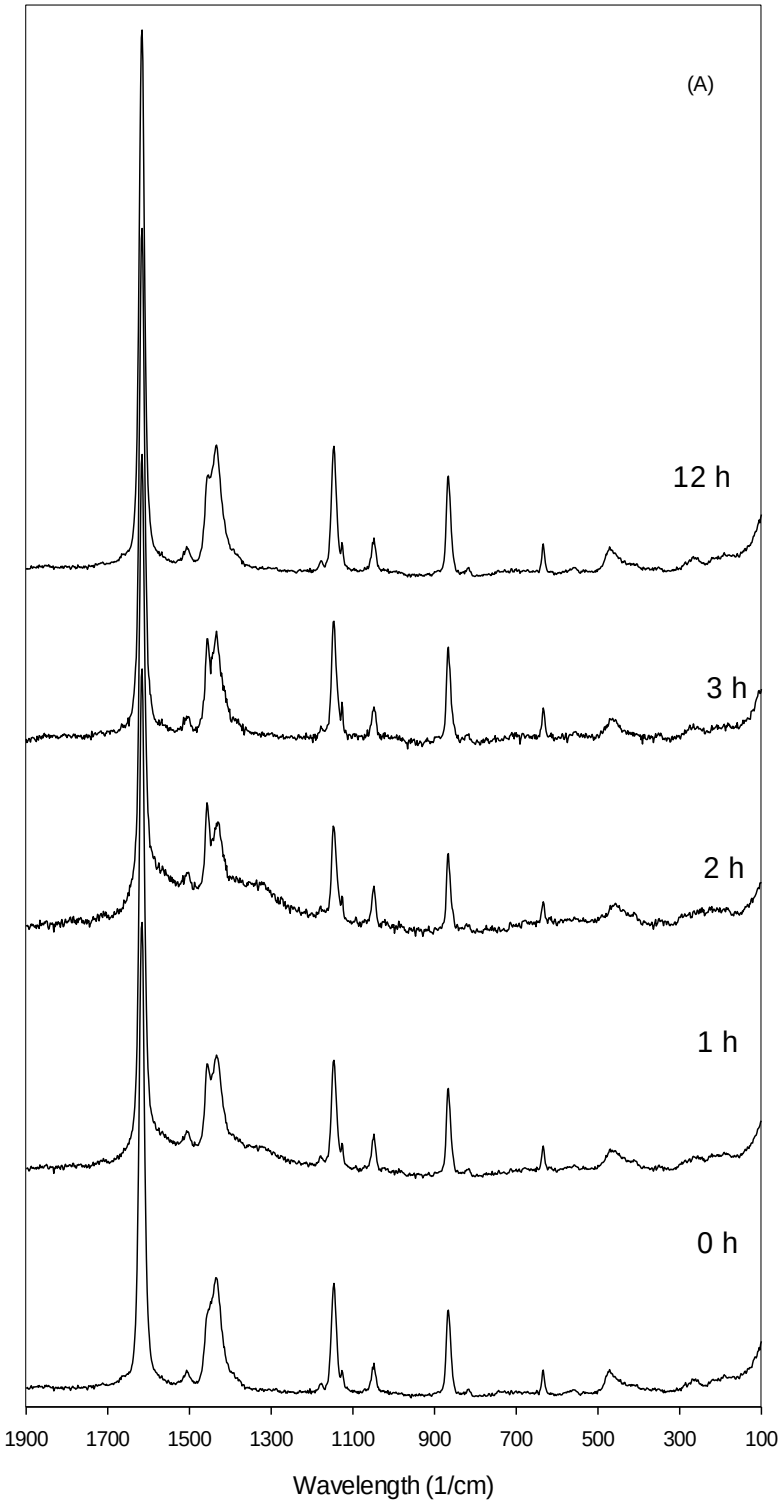


Fig. S2 UV-Vis spectra of Fe_2Ni-NO_3-x (A) and Fe_2Ni-Cl-x (B) samples prepared using $Fe(NO_3)_3.9H_2O$ and $FeCl_3.6H_2O$, respectively at different synthesis times

2. Raman spectra



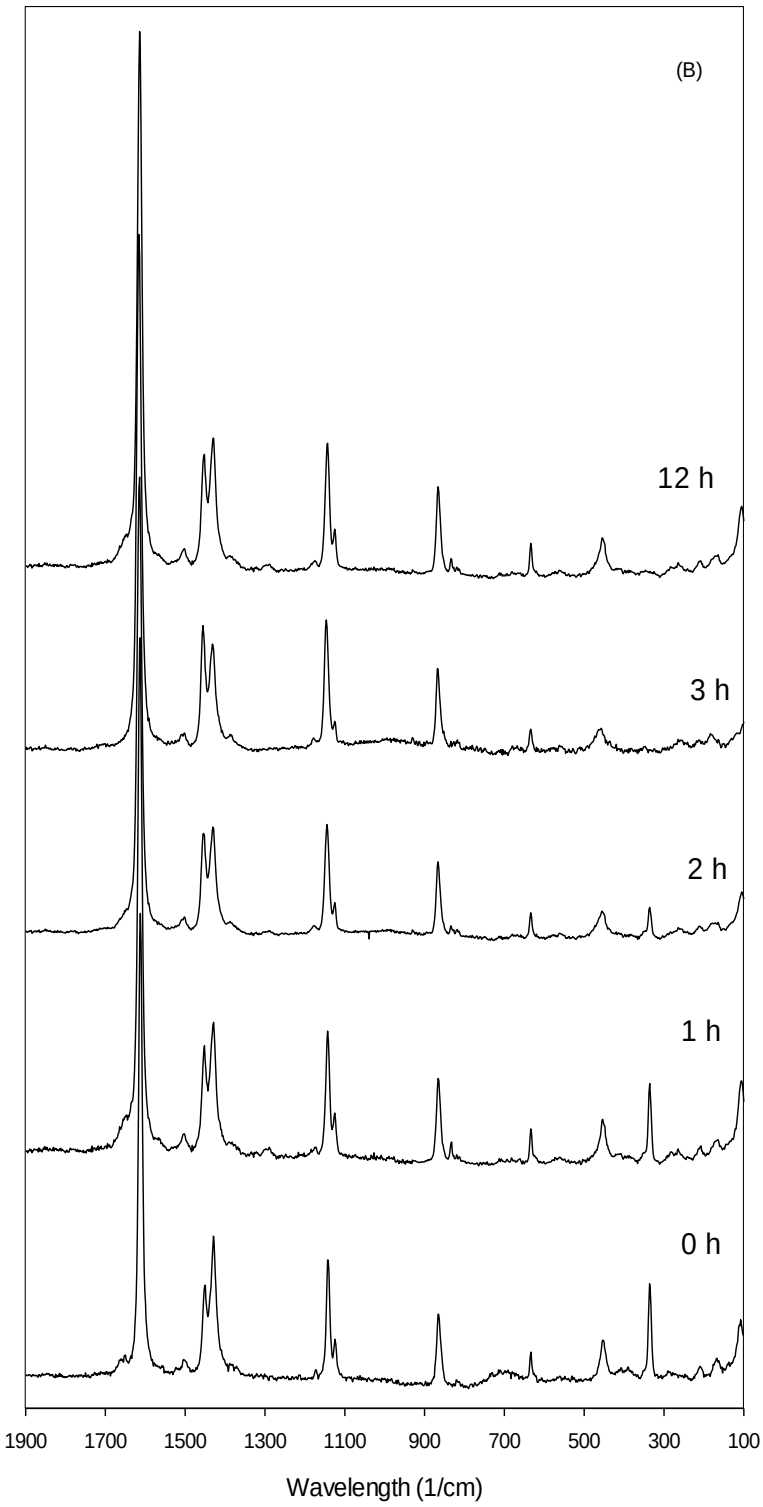
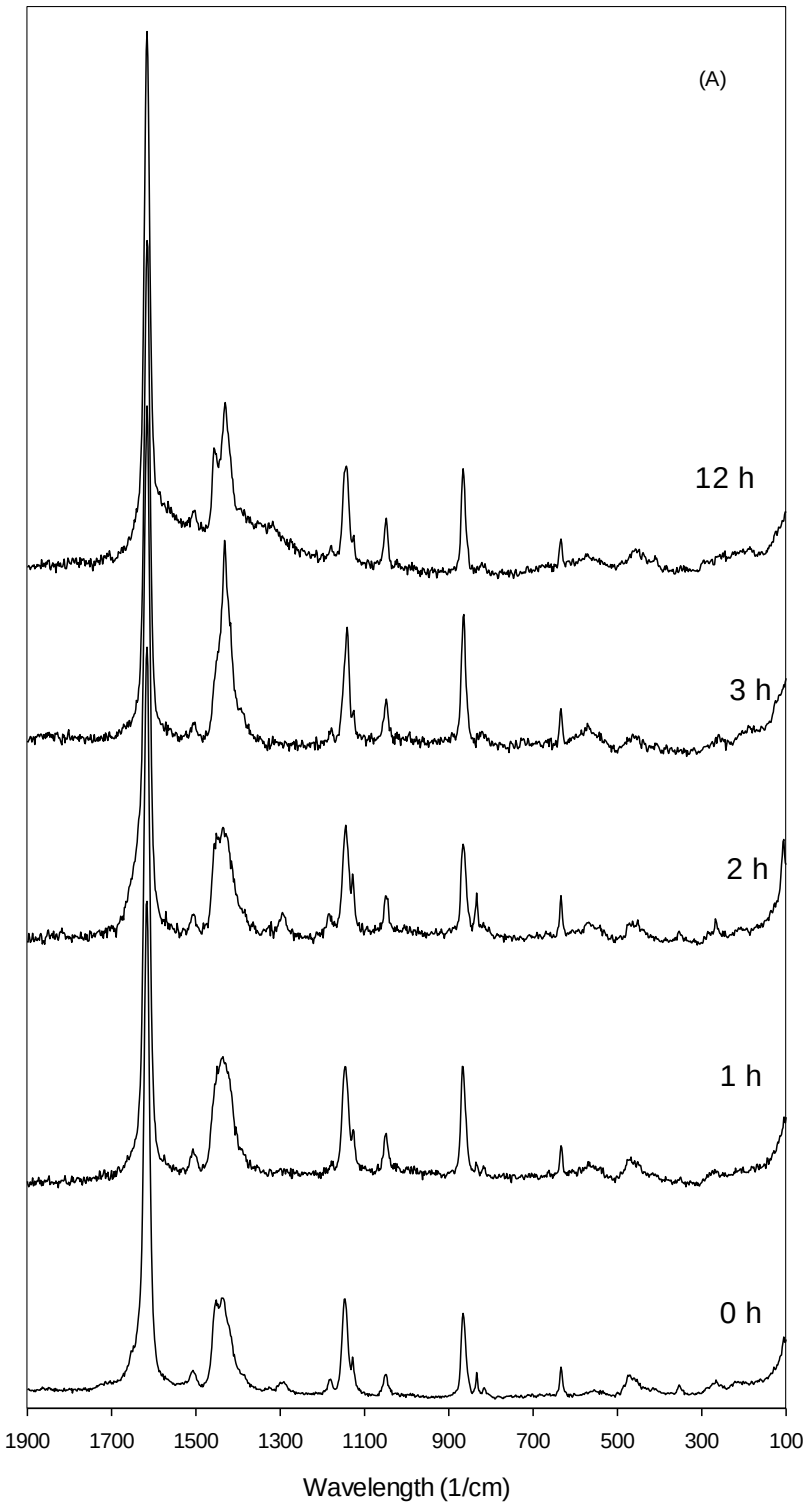


Fig. **S3** Raman spectra of the samples Fe_3-NO_3-x (A) and Fe_3-Cl-x (B) at different synthesis times



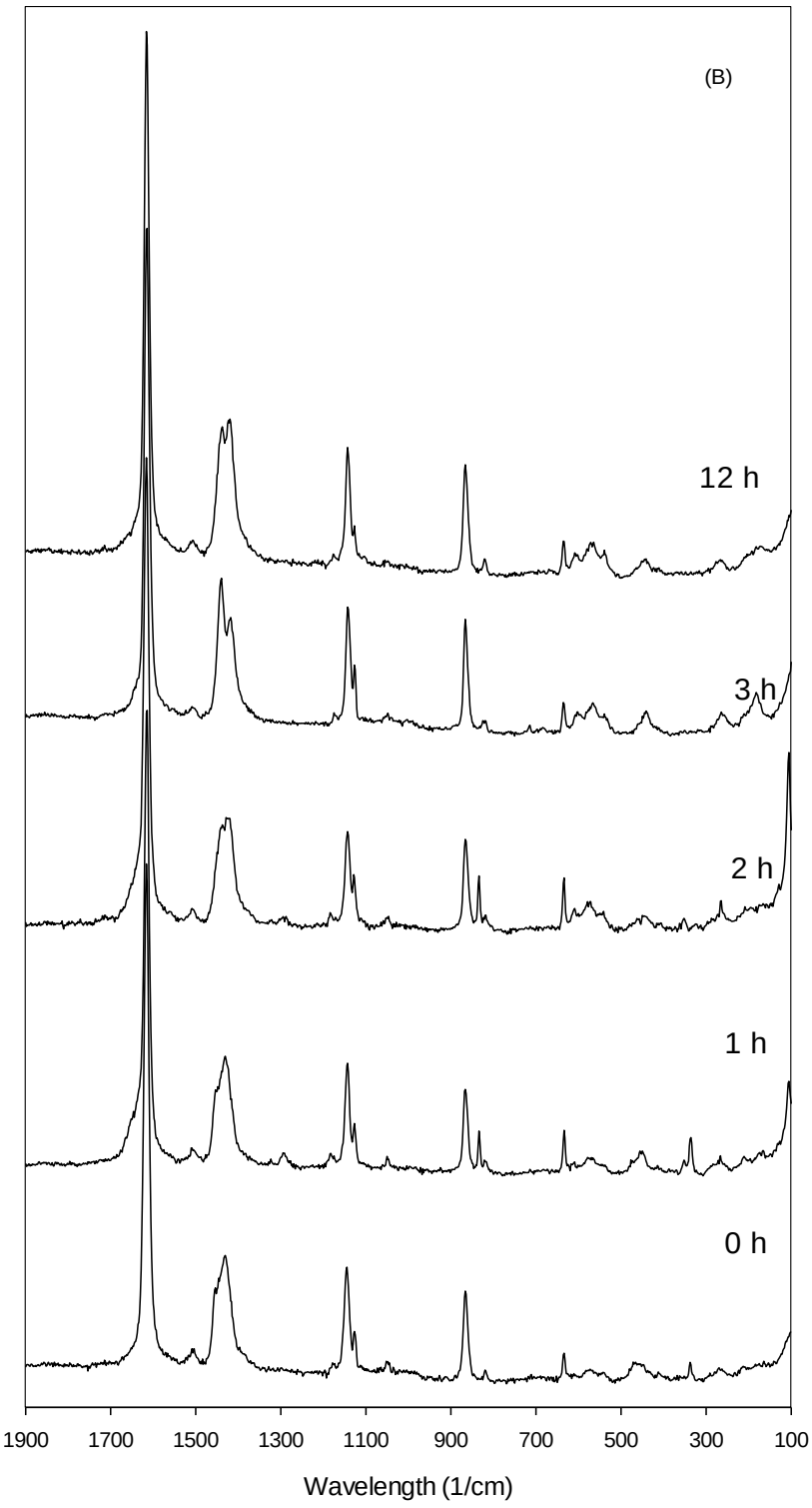
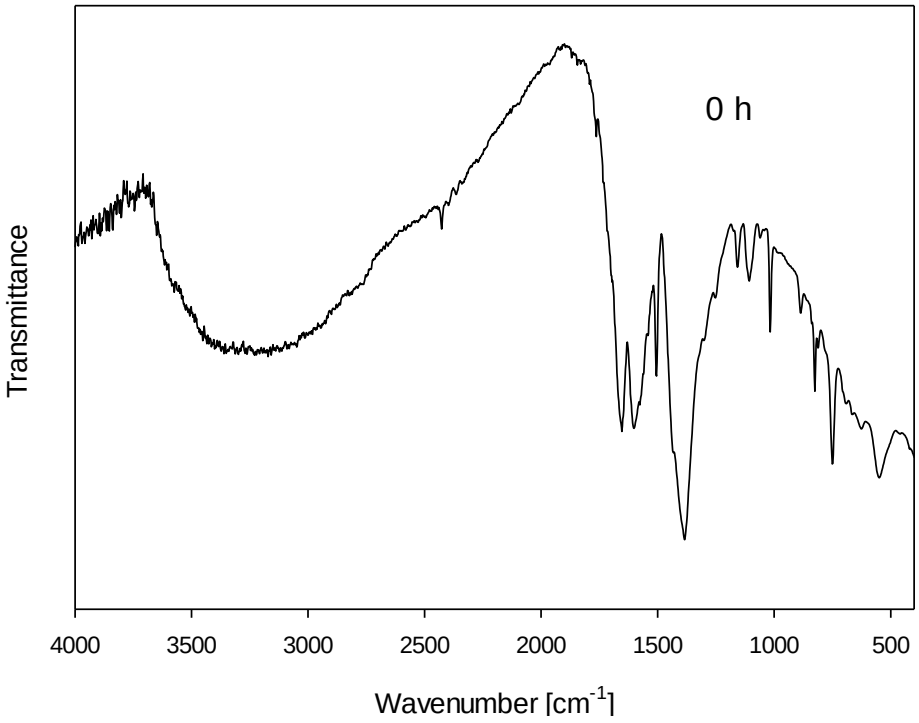
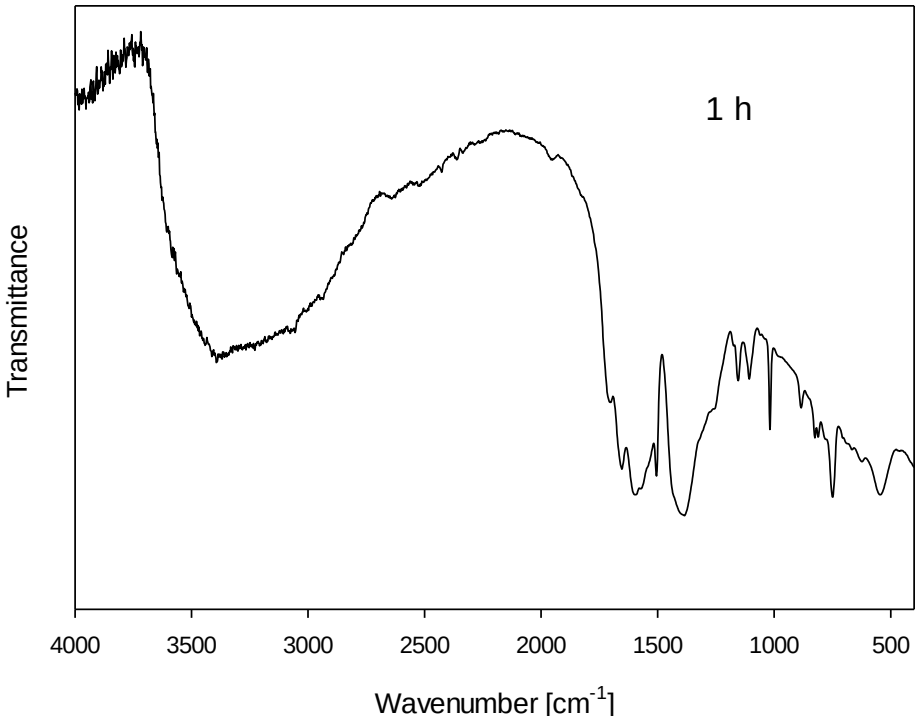


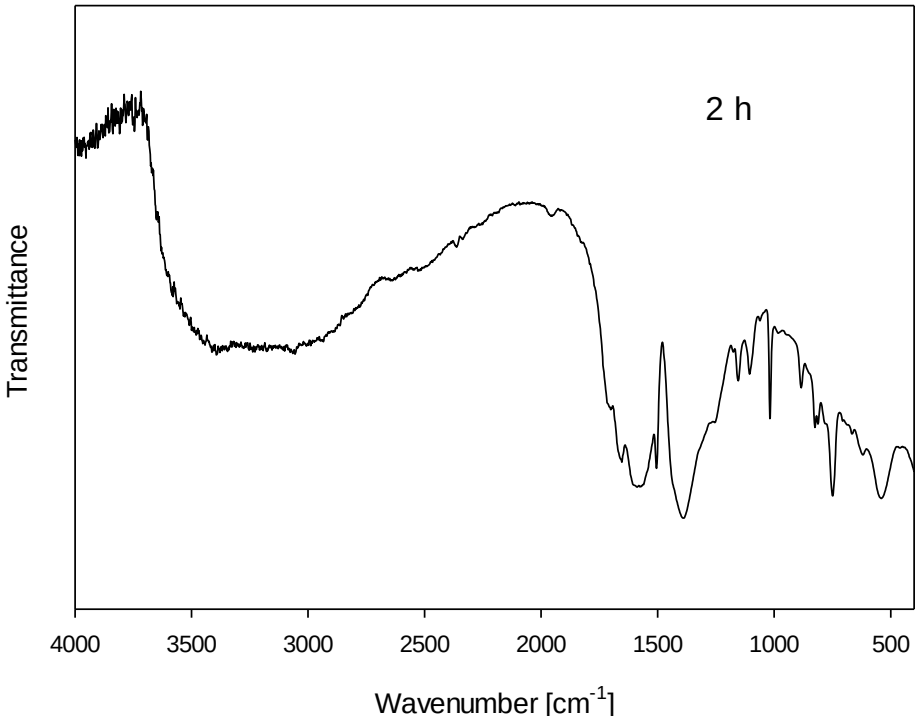
Fig. S4 Raman spectra of Fe_2Ni-NO_3-x (A) and Fe_2Ni-Cl-x (B) at different synthesis times.

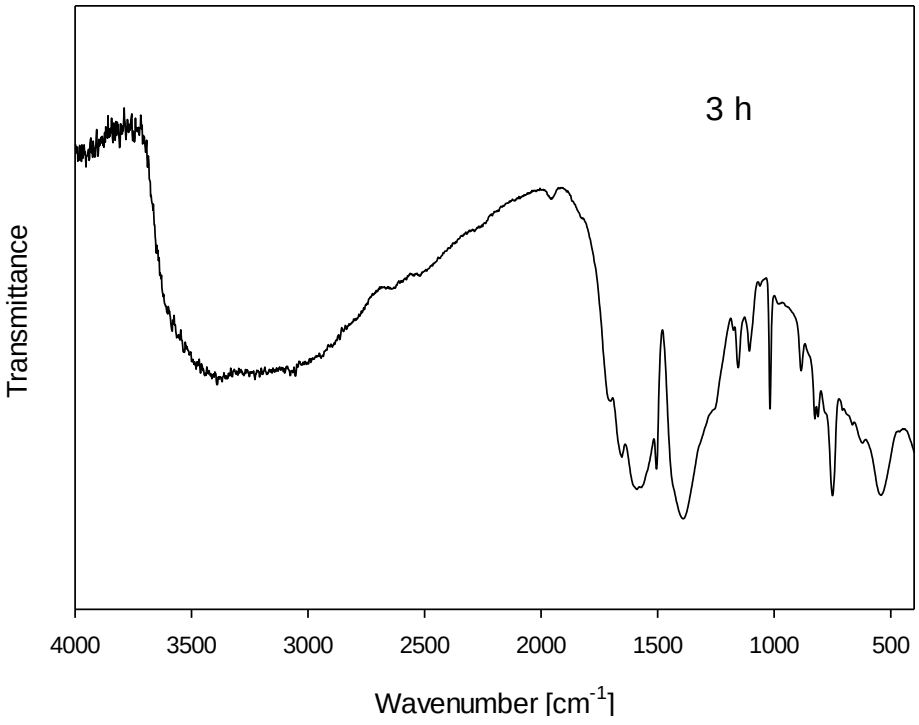
3. FTIR spectra of samples with wavelength 400 – 4000 cm^{-1}

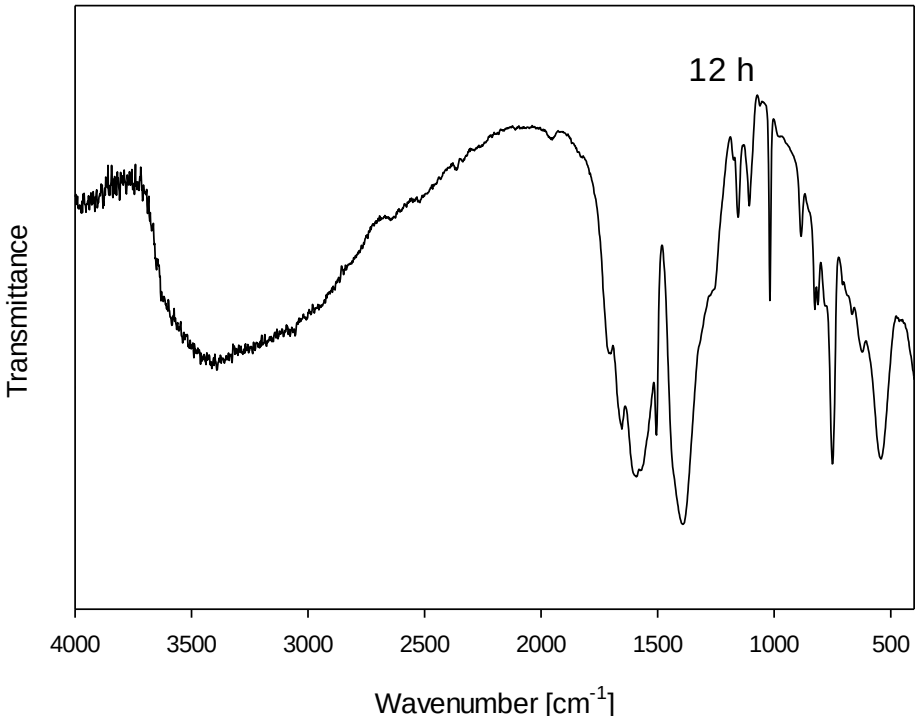
3.1. Single metal synthesis using $Fe(NO_3)_3.9H_2O$



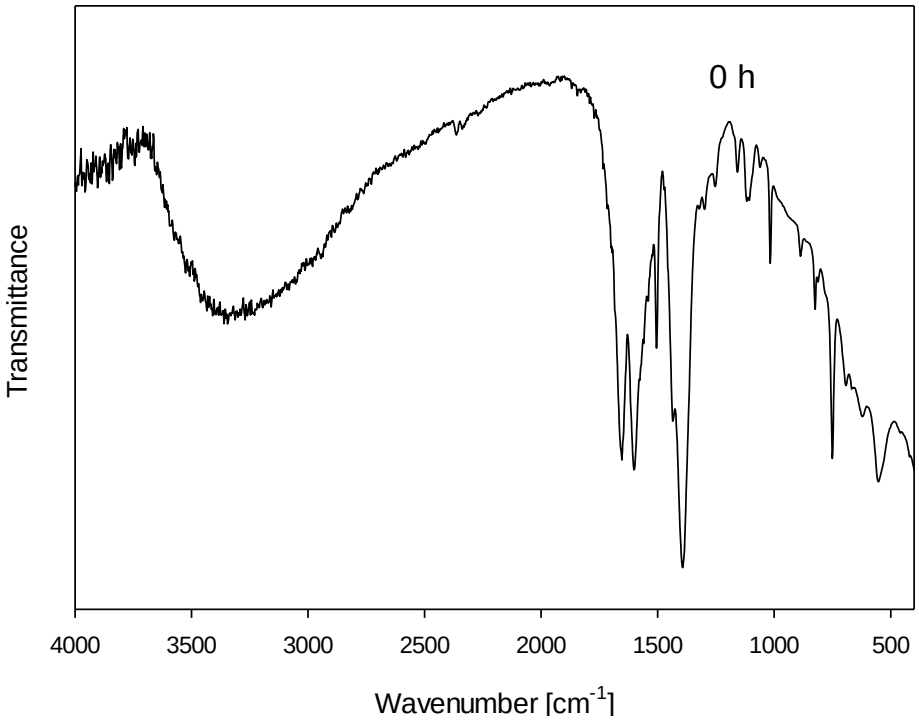


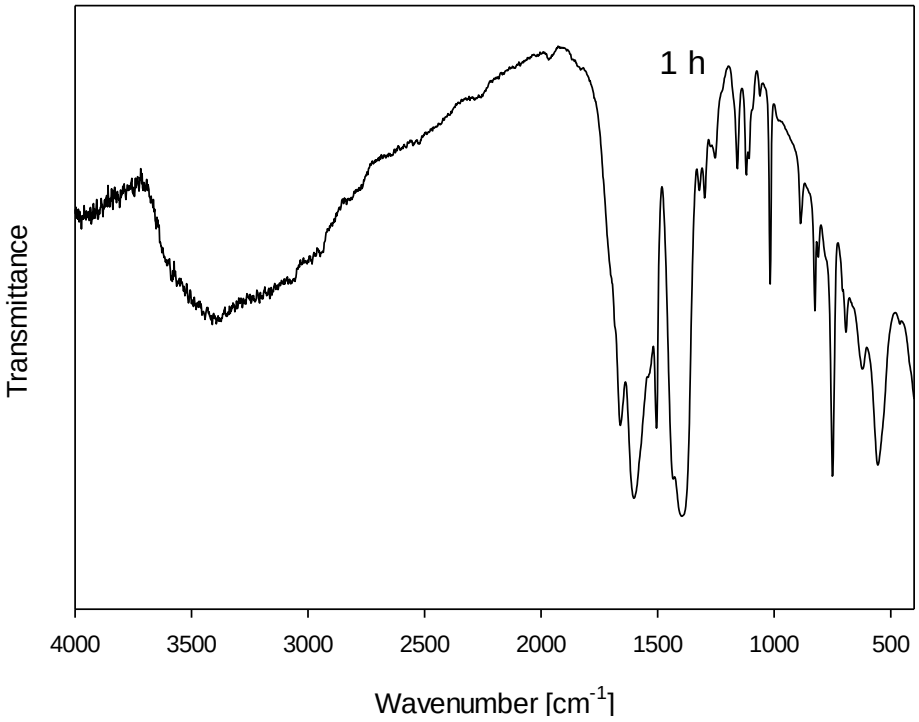


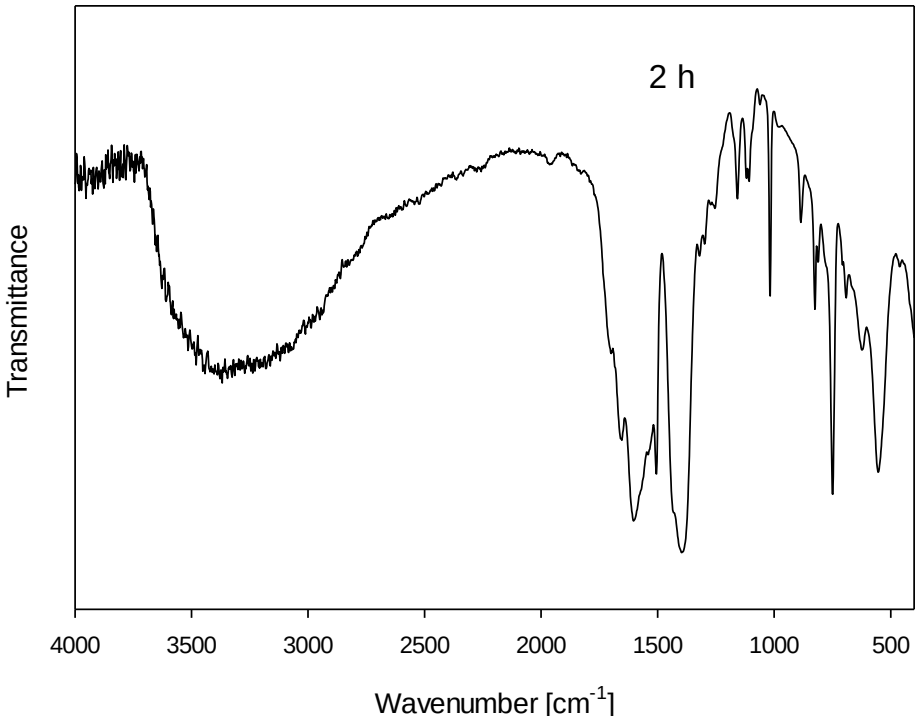


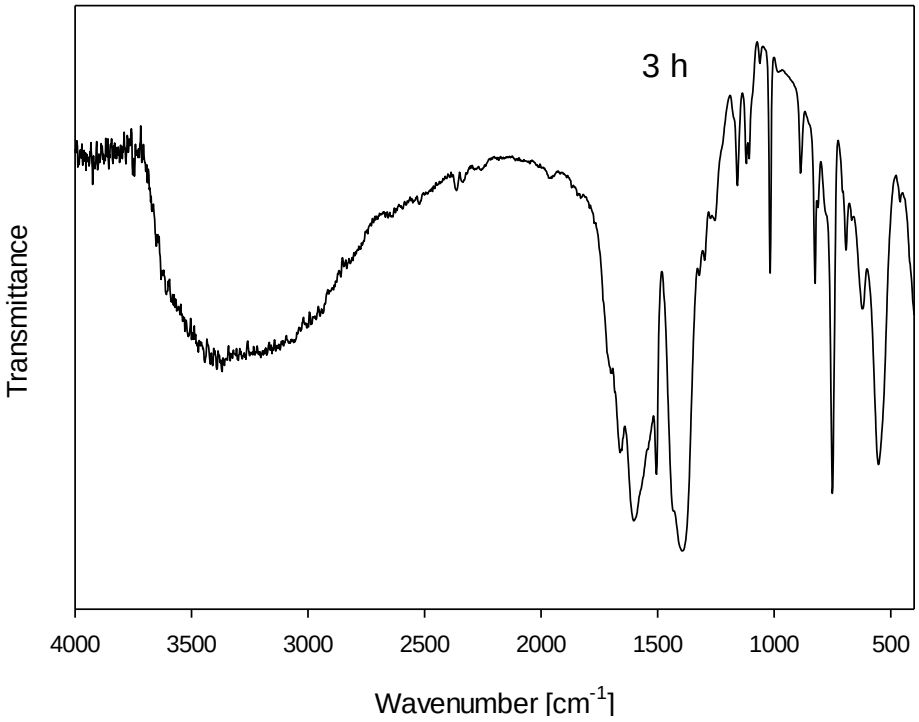


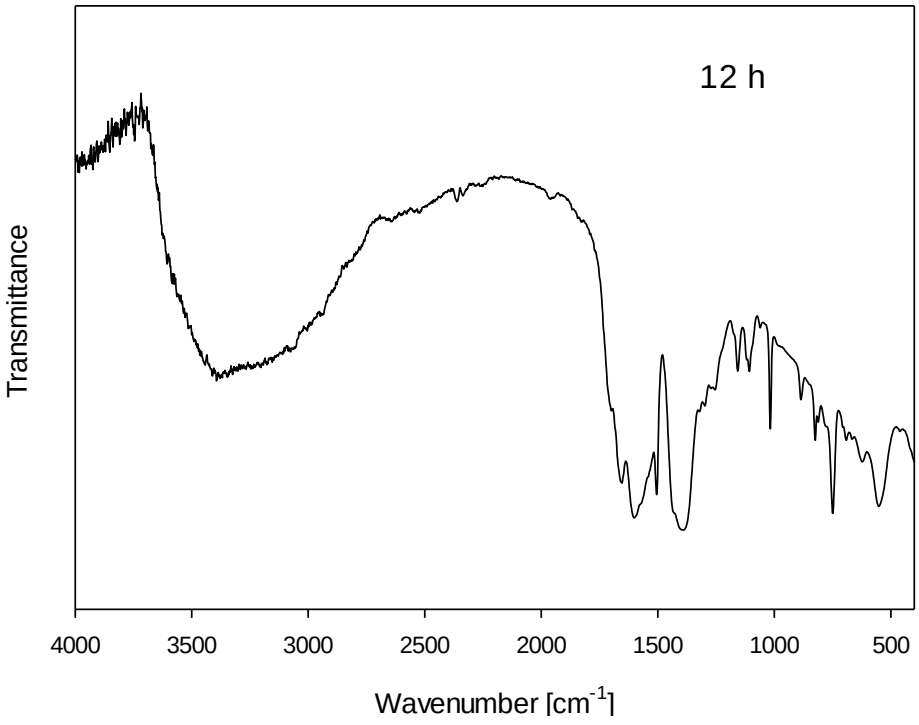
3.2. Single metal synthesis using $FeCl_3.6H_2O$



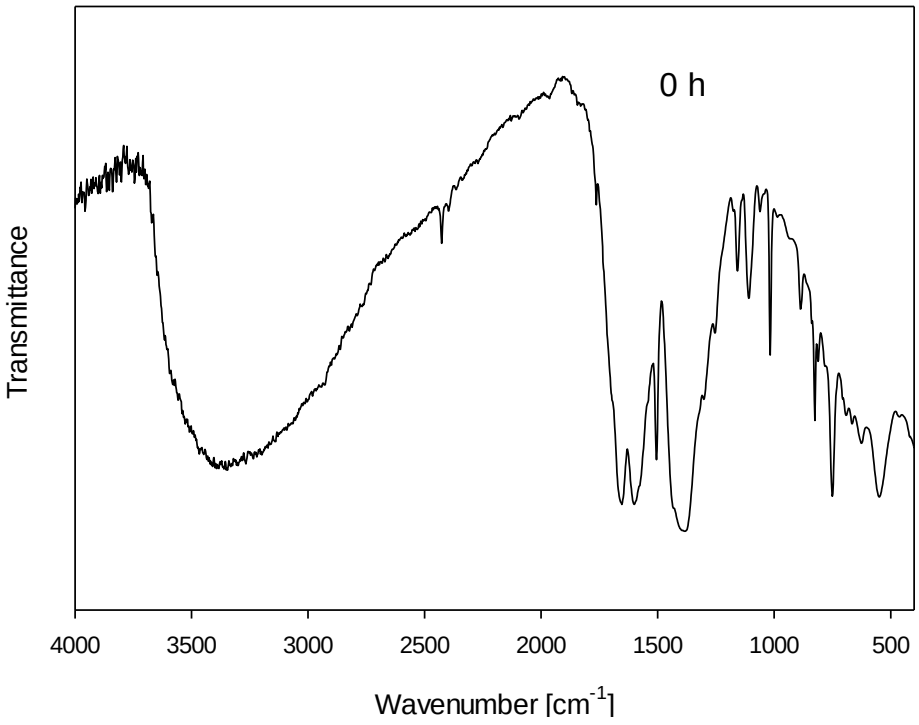


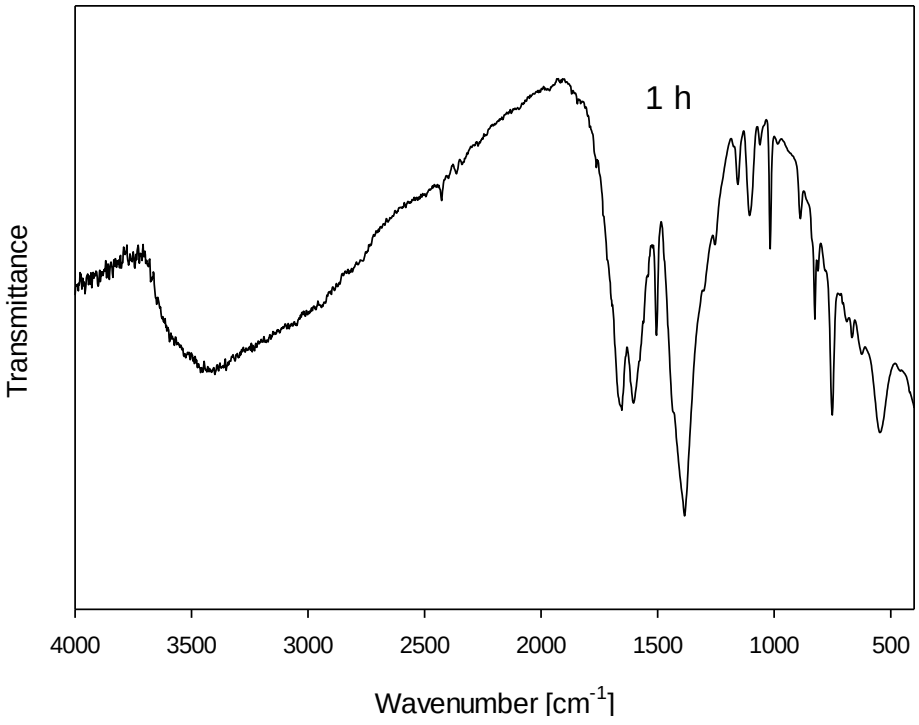


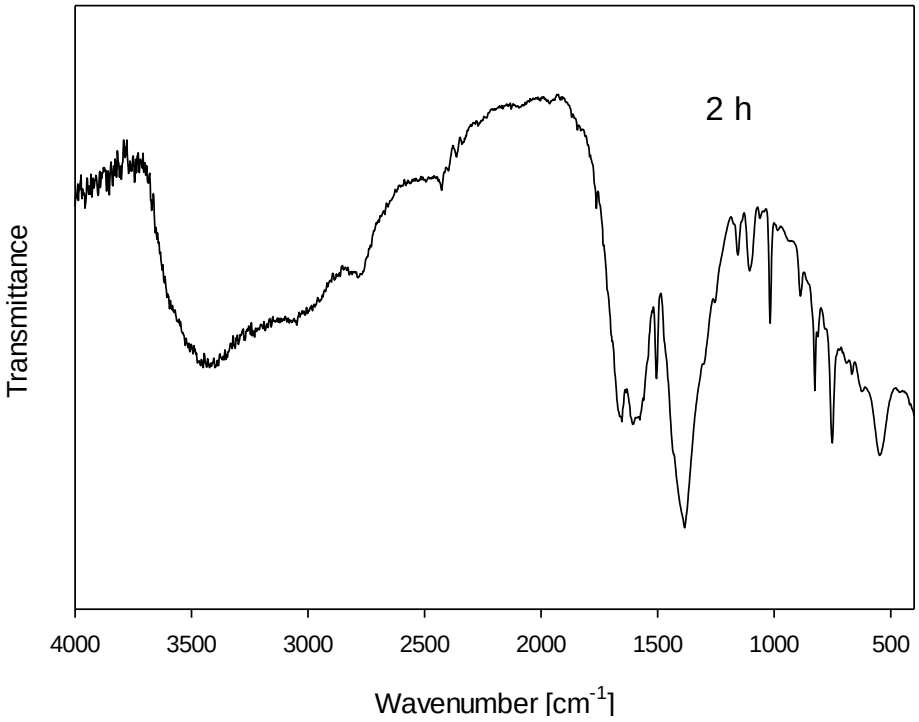


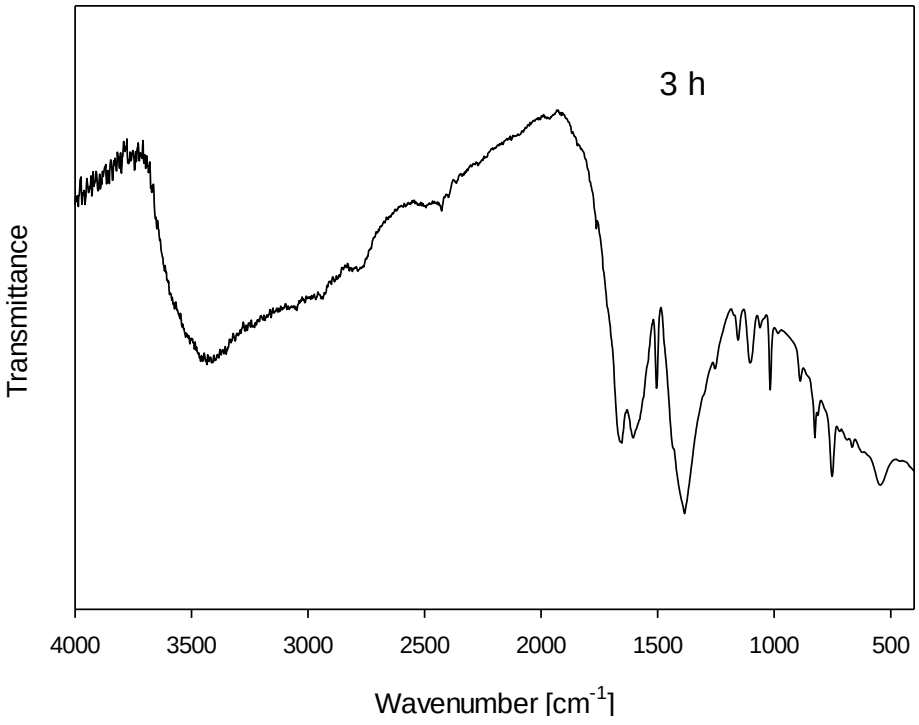


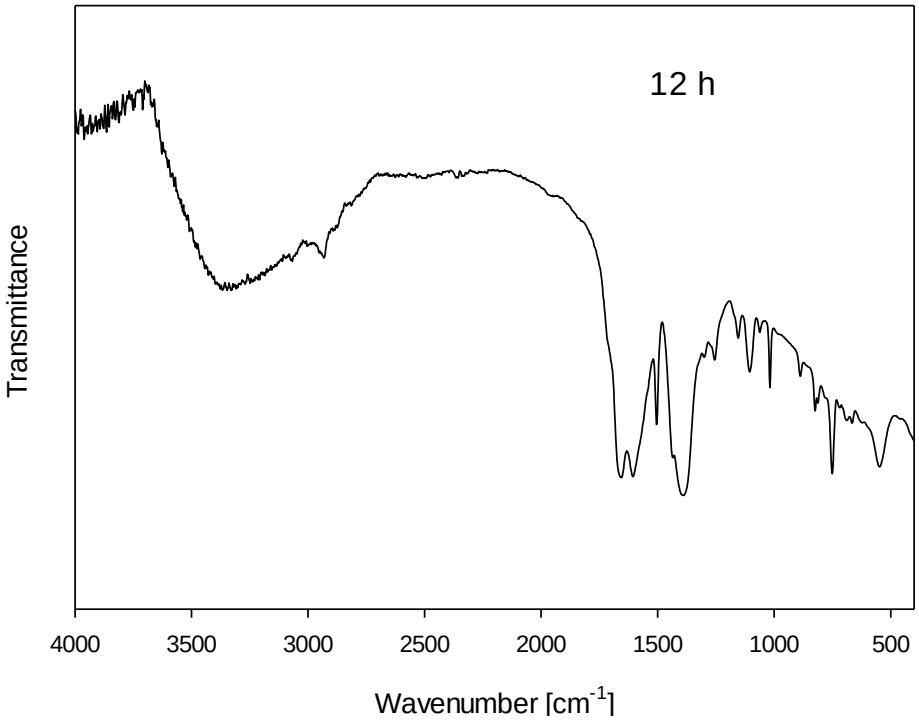
3.3. Mixed metal synthesis using $Fe(NO_3)_3.9H_2O$



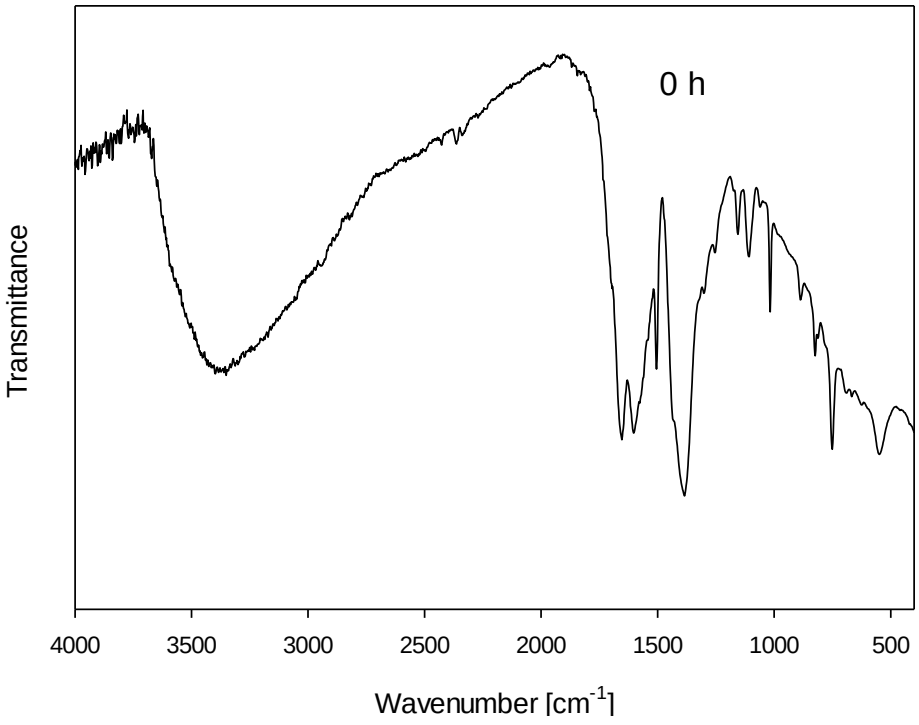


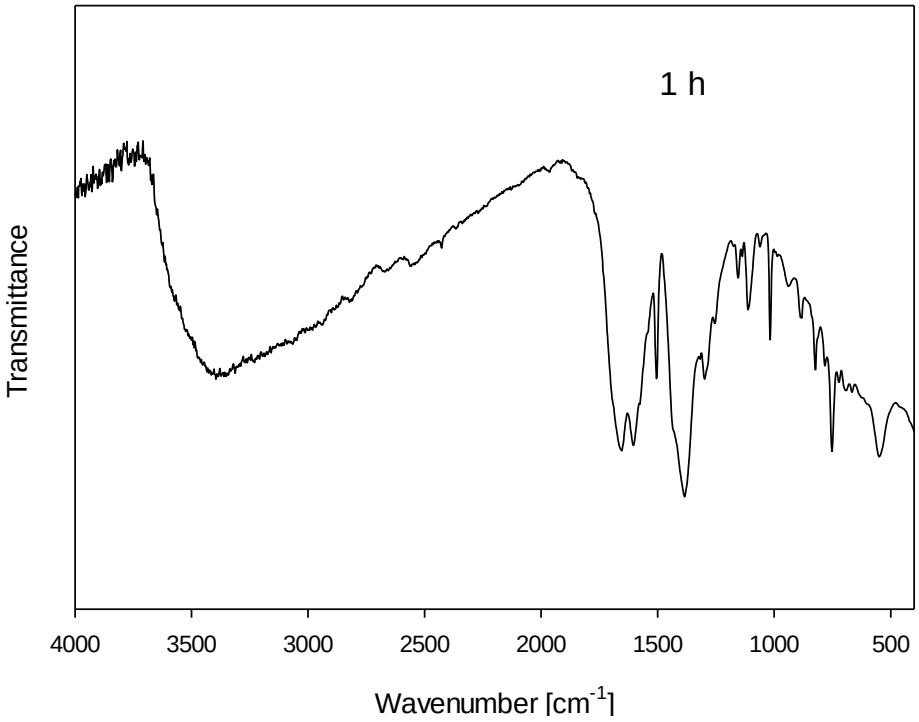


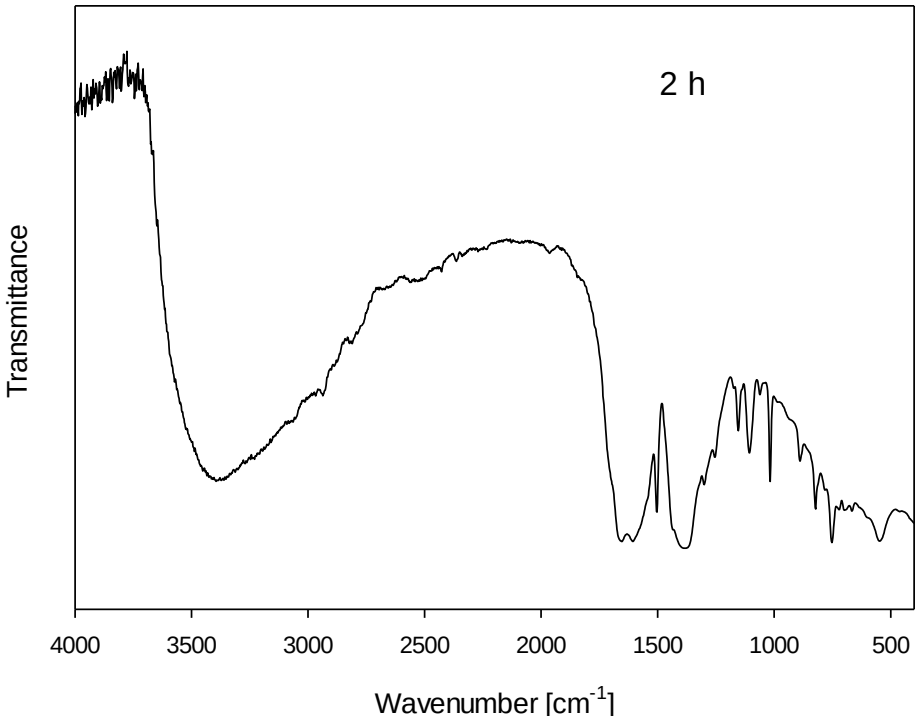


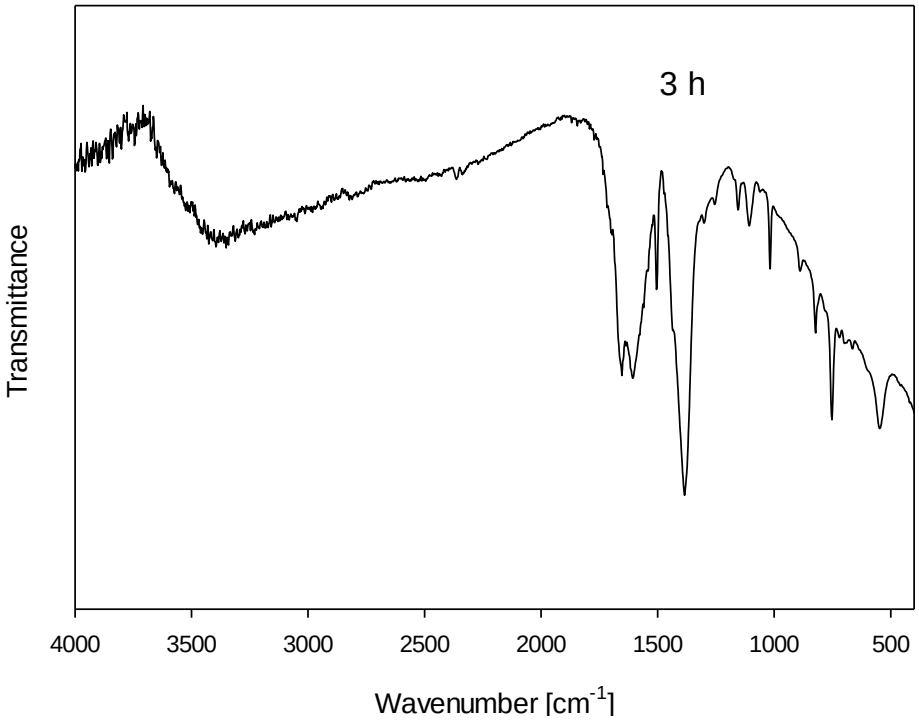


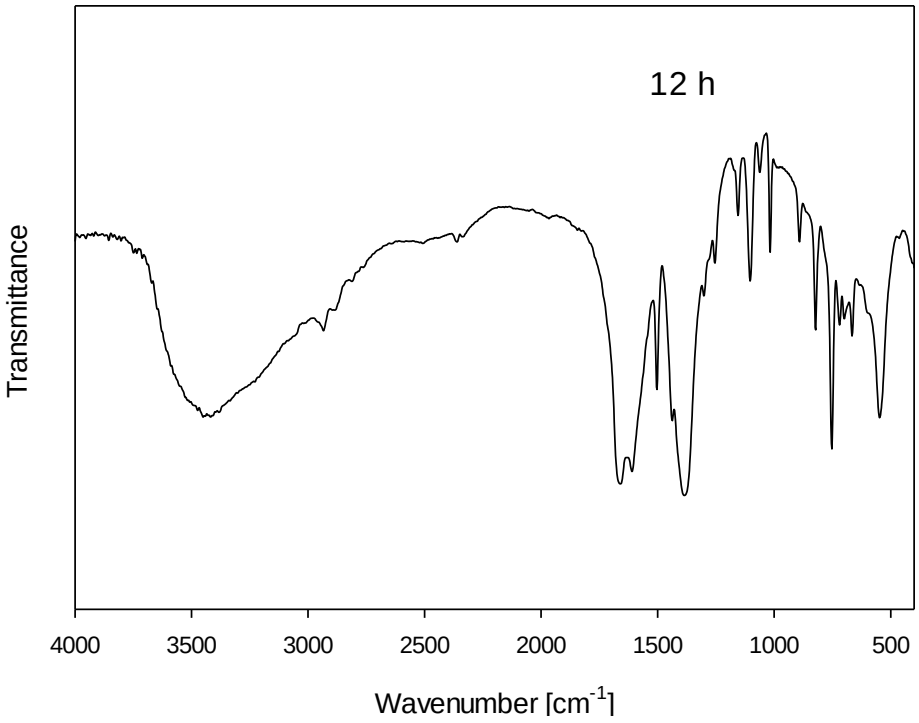
3.4. Mixed metal synthesis using $FeCl_3.6H_2O$







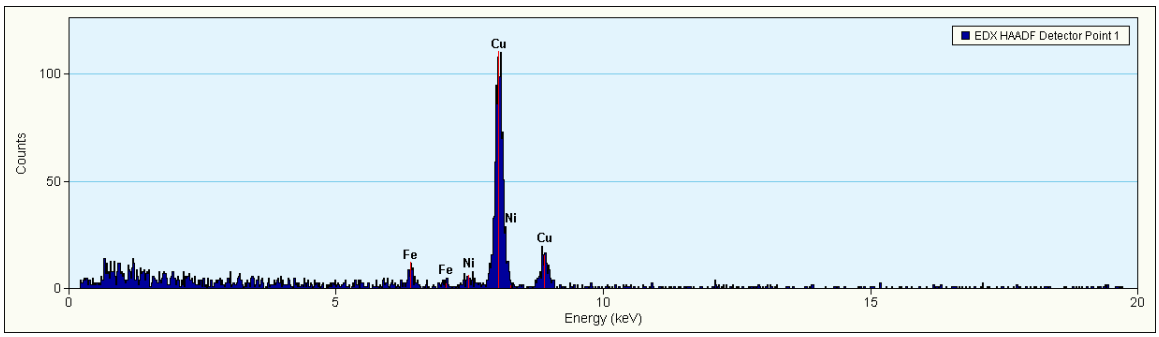




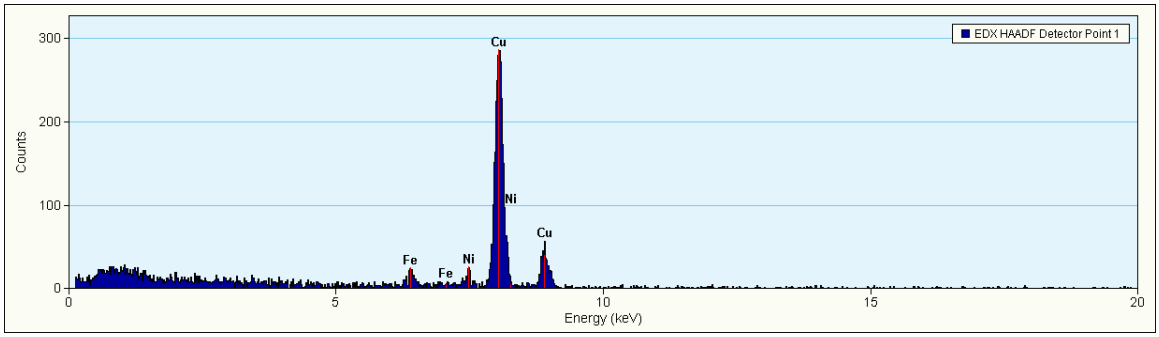
4. HRTEM and EDS analysis

EDS spectra of 5 positions taken on the same Fe_2Ni-MIL-88B crystal (see Figure 9 in the article).

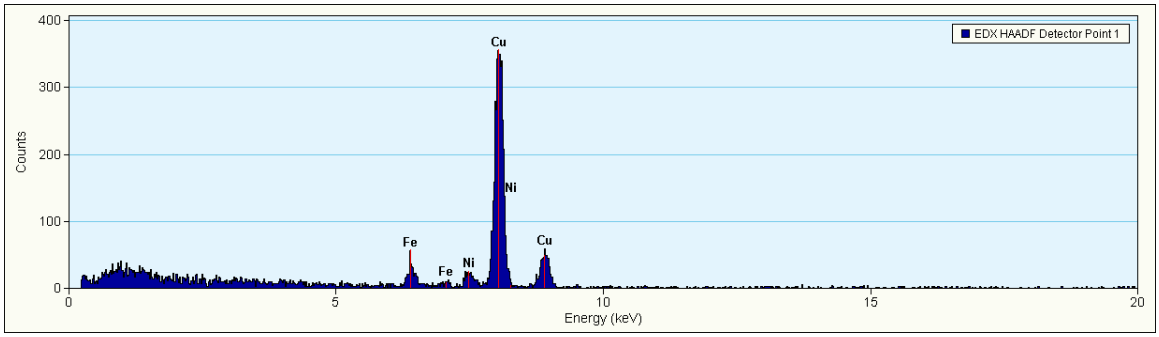
Since the samples were dispersed on a copper grid for analysis. Signal of copper was observed in the EDS spectra.



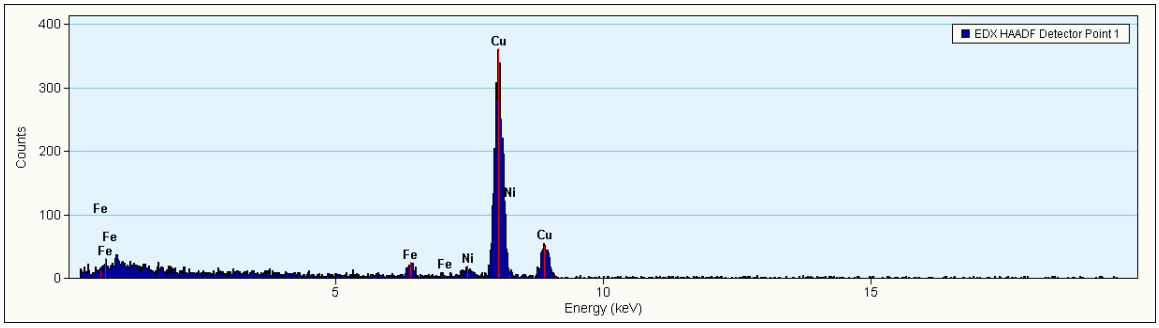
EDS spectroscopy of position 1



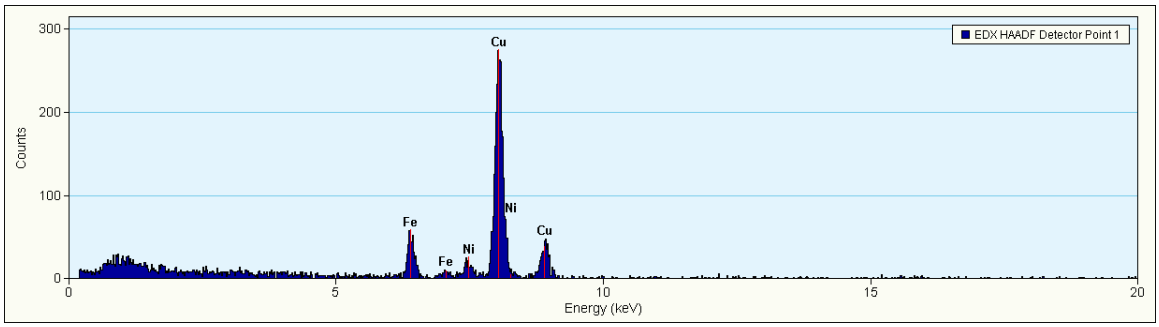
EDS spectroscopy of position 2



EDS spectroscopy of position 3



EDS spectroscopy of position 4



EDS spectroscopy of position 5

5. XPS analysis of Fe_2Ni-MIL-88B-12h, dried

The X-ray photoelectron spectra (XPS) were taken on a photoelectron spectrometer (KRATOS AXIS-ULTRA) with a monochromatic X-ray source of Al Kα . The operating conditions for recording high-resolution spectra were as follows: 1486.6 eV and 225 W; pass energy of 160 eV with anoperating pressure of 10^{-9} Torr.

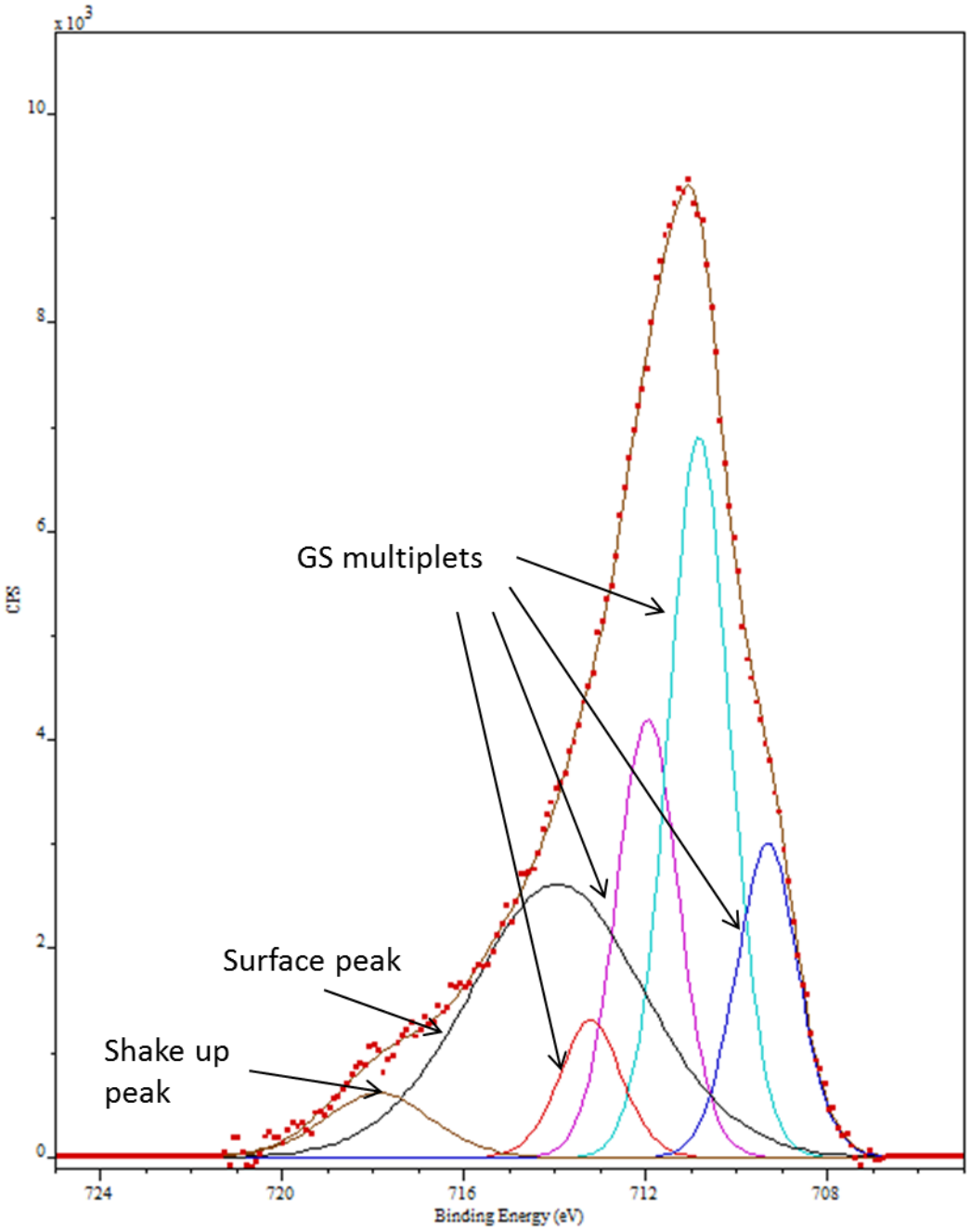
CasaXPS software was use to analys the collected XPS spectra. [1] All spectra were calibrated using the adventitious C 1s peak with a fixed value of 284.8 eV. Shirley background was then applied and subtracted.

As the Fe cation in trinuclear cluster is at high spin state,[2,3] envelope of Fe $2p_{3/2}$ spectrum was fit with peaks corresponding to the GS multiplets, surface structures and shake-up-related satellites.[4-6] All the four GS multiplets have the same full width at half-maximum (FWHM) of 1.6 eV and their peak areas are in similar to those of multiplets. The rest of the envelop was filled with one surface structure peak and one satellites peak.

Fitting result is in agreement with Fe^{3+} GS multiplets , suggesting the presence of only Fe^{3+} not Fe^{2+} in the sample.

Gupta and Sen (GS) multiplet peak parameters used to fit the high-spin Fe^{3+}

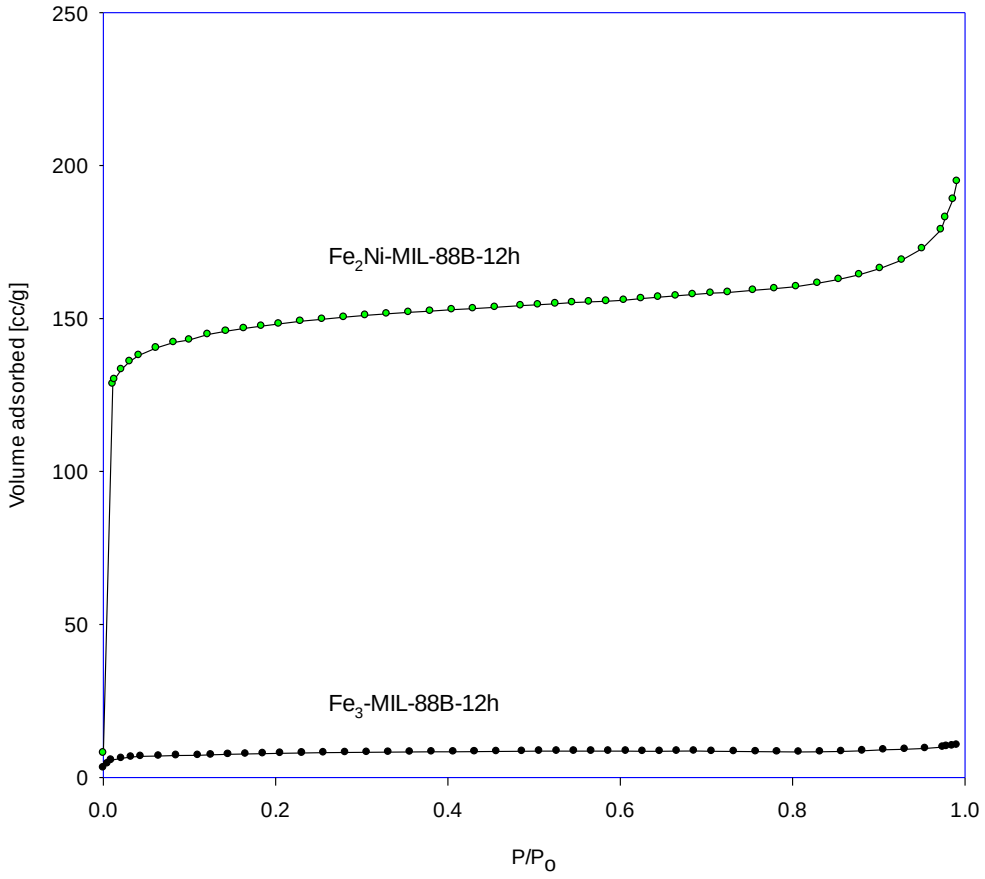
Sample	Peak 1			Peak 2			Peak 3			Peak 4		
	eV	% area	ΔE	eV	% area	ΔE (eV)	eV	% area	ΔE (eV)	eV	% area	ΔE (eV)
Fe_2Ni-MIL-88B-12h	713.2	7	1.3	711.9	21	1.1	710.8	35	1.5	709.3	37	
GS Fe3+ multiplets		10	0.6		20	1.3		30	1.6		40	



6. Adsorption analysis

N_2 adsorption analysis and was carried out in an Autosorb 1 instrument, before analysis the samples were outgassed in a vacuum for 3 h at 150 °C. Specific surface area was calculated with the BET model in the linear range of P/Po = 0 – 0.15

Sample	Specific surface area m^2/g
Fe2Ni-MIL-88B-12h	350
Fe3-MIL-88B-12h	5



References

1. Fairley N. CasaXPS Version 2.2.19, copyright 1999–2003
2. Boudalis A. K. et al *Polyhedron* **2005**, *24*, 1540
3. Psycharis, V et al *Eur. J. Inorg. Chem* **2006**, *2006*, 3710-
4. Gupta RP, Sen SK. *Phys. Rev. B.* **1975**; *12*: 15
5. Grosvenor A.P et al. *Surf. Interface Anal*. **2004**, *36,* 1564
6. Mullet M. et al. *Surf. Interface Anal*. **2008**, *40*, 323