Supplementary Information (SI) for RSC Mechanochemistry.
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Supporting Information

Encapsulation of (pseudo)halogen metal complexes in zeolite Y cages by mechanochemistry

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Materials and Methods

Materials

The reagents were used as received from the supplier without further purification: starting FAU-type zeolite Y (ZY, Silkem, sodium form, Si/Al = 2.6); nickel(II) chloride hexahydrate ($NiCl_2·6H_2O$, 99%; Fischer Scientific), cobalt(II) nitrate trihydrate ($Co(NO_3)_2·3H_2O$, 99%; VWR Chemicals), cobalt(II) chloride hexahydrate ($CoCl_2·6H_2O$, 96%; Fischer Chemical) iron(II) sulphate heptahydrate ($FeSO_4·7H_2O$, p.a.; Kemika), copper(II) nitrate trihydrate ($Cu(NO_3)_2·3H_2O$, p.a.; Kemika), potassium cyanide (96%; Sigma Aldrich), potassium iodide (p.a.; Kemika), elemental iodine (p. a.; Kemika) and the reference potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6]·3H_2O$, 99%; Kemika). Doubly distilled water was used for all aspects of this research (synthesis and sample washing). Absolute ethanol was used for washing of samples containing elemental iodine (ZY-M-I_2; M = Fe, Co, Ni, Cu).

Methods

Mechanochemical synthesis

Milling was carried out in a vibrational ball mill (Retsch MM400) at a frequency of 25 Hz for 30 minutes in 13 ml poly(methyl methacrylate) (PMMA) jars with a single zirconium oxide (ZrO_2) ball (4 mm in diameter) without adding any additional solvent. 0.2 g of zeolite Y was mixed with 0.35 g of metal salts ($NiCl_2·6H_2O$, $Co(NO_3)_2·3H_2O$, $FeSO_4·7H_2O$, $Cu(NO_3)_2·3H_2O$),and milled for 30 minutes to ensure qualitative ion-exchange. After grinding, the samples were washed in water to remove any leftover salts on the zeolite surface. The washing step was carried out three times by suspending modified zeolites in water and then separating them using a centrifuge. Modified zeolites were then dried overnight in an oven at a temperature of 80 °C. The metal-modified samples (0.1 g) were then mixed with a 1:6 stoichiometric ammount of potassium cyanide, potassium iodide or elemental iodide (with the assumption that 100% of metal was exchanged in the initial modification) and milled for another 30 minutes. The same washing and drying procedure was repeated. Samples containing elemental iodine were washed with ethanol rather than water.

Preparation of reference samples

To obtain reference C≡N IR bands wavelengths for known cyanide complexes, potassium hexacyanocobaltate(III) ($K_3[Co(CN)_6]$) and sodium tetracyanonickelate(II) ($Na_2[Ni(CN)_4]$) were prepared by solution-based methods. $K_3[Co(CN)_6]$ was prepared in a two-step process. First, an aqeous solution of cobalt(II) chloride hexahydrate (4 g in 40 mL of water) was reacted with a solution of potassium cyanide (2.5 g in 17 mL of water). The brown precipitate was filtered out, dissolved in water and further reacted with another portion of potassium cyanide (5 g in 14.5 mL) and stirred until the mixture became pale yellow. Yellow crystals of $K_3[Co(CN)_6]$ were obtained within one week. $Na_2[Ni(CN)_4]$ was prepared similarly to the cobalt(III) complex. A solution of nickel(II) chloride hexahydrate (2.9 g in 20 mL of water) was reacted with a solution of sodium cyanide (1.4 g in 20 mL of water). The grey-green precipitate was filtered out, dissolved in 2 mL of water and reacted with another portion of sodium cyanide (1.4 g in 3 mL of water). The orange solution yielded crystals of $Na_2[Ni(CN)_4]$ within one week.

Theoretical simulations

In order to identify the products, potential complexes were constructed in GaussView 6.0.16 and simulated in Gaussian 09 revision-D.01. Furthermore, simulations of their far-IR spectra were carried out by hybrid DFT functional WB97XD with the 3-21G* basis set. Optimisation of the built structure was carried our first, taking care to ensure the charge of the molecule was correct. Afterwards, frequency was simulated for both IR and Raman spectra with anharmonic corrections until convergence was achieved. Obtained spectra was compared with experimental data. This was carried out with a trial-error system, until good correspondence (within +/- 4 cm^{-1}) to experimental spectra was found.

Preparation of corrosive gas atmospheres

HCl saturated atmosphere was obtained by adding 5 ml of concentrated hydrochloric acid to a 1 dm^3 glass bottle and then agitating it until it was filled with fumes of HCl. NO_2 saturated atmosphere was produced by reacting 1 g of copper wire with 4 ml of concentrated nitric acid (HNO_3) in a 0.5 dm^3 glass bottle.

Characterization

PXRD patterns of the samples were collected using PANalytical Aeris benchtop powder diffractometer (CuKα radiation with Ni filter; λ= 1.5418 Å, 45 kV, 40 mA) in Bragg-Brentano geometry in a 5°-50° 2ϑ range (0.025° step). Particle size distribution (PSD) curves were obtained by laser light scattering analysis using Malvern Mastersizer 2000 laser light scattering granulometer. The samples were exposed to ultrasonication during the measurement to prevent agglomeration. Scanning electron microscopy (SEM) images were acquired on a Jeol JSM 7000F scanning electron microscope. The energy dispersive X-ray spectra (EDS) were recorded with a coupled Oxford INCA Energy 350 spectrometer. Mid-IR spectra were collected on a PerkinElmer Frontier FTIR spectrometer with an attenuated total reflection (ATR) addon in the range of 4000-400 cm^{-1}. Far-IR spectra were collected on a ThermoFisher Nicolet iS50 FTIR spectrometer with an ATR add-on in the range of 800-110 cm^{-1}. Solid-state UV-Vis spectra were obtained by measurement on a Thermo Scientific Evolution 350 UV-Vis spetrometer. Data was visualized in MagicPlot Student and Spectragryph software packages.

Supplementary tables

Table S1 C≡N vibrations for alternative cyanide products from the reference 26 in the main text.

	ν_{exp} (cm^{-1})
$[Fe(CN)_6]^{3-}$	2116
$[Co(CN)_6]^{4-}$	-*
$Ni(CN)_2$	2176

* According to literature reports,[26] the Co(II) cyanide complex is highly unstable and its IR spectrum has not been measured.

Table S2 Vibration values for HCl and NO_2 captured by the samples measured by IR.

Sample	ν_{HCl} (cm^{-1})	ν_{NO2} (cm^{-1})
ZY (starting material)	3044	1355
ZY-Fe	3041	1356
ZY-Fe-I_2	-	1349
ZY-Fe-KI	-	1348
ZY-Fe-CN	3054	1352
ZY-Co	3042	1321
ZY-Co-I_2	-	1351
ZY-Co-KI	-	1320
ZY-Co-CN	3044	1367
ZY-Ni	3041	1336
ZY-Ni-I_2	3036	1341
ZY-Ni-KI	3033	1375
ZY-Ni-CN	3036	1376

ZY-Cu	3043	1328
ZY-Cu-I_2	3036	1337
ZY-Cu-KI	-	1319

Table S3 Values under which 50% of particles lie in the particle size distribution by number ($D_{(N0.5)}$) and volume ($D_{(V0.5)}$) measured by LLS for the obtained samples.

Sample	**$D_{(N0.5)}$ (µm)**	**$D_{(V0.5)}$ (µm)**
ZY (starting material)	1.262	2.910
ZY-Fe	0.791	3.950
ZY-Fe-I_2	0.839	2.293
ZY-Fe-KI	0.803	2.681
ZY-Fe-CN	0.918	1.600
ZY-Co	1.216	2.163
ZY-Co-I_2	0.935	2.186
ZY-Co-KI	0.968	2.064
ZY-Co-CN	0.955	2.180
ZY-Ni	0.977	2.062
ZY-Ni-I_2	0.860	2.281
ZY-Ni-KI	0.916	1.864
ZY-Ni-CN	0.937	2.112
ZY-Cu	0.960	1.820
ZY-Cu-I_2	0.954	2.384
ZY-Cu-KI	0.702	1.790

Supplementary Figures

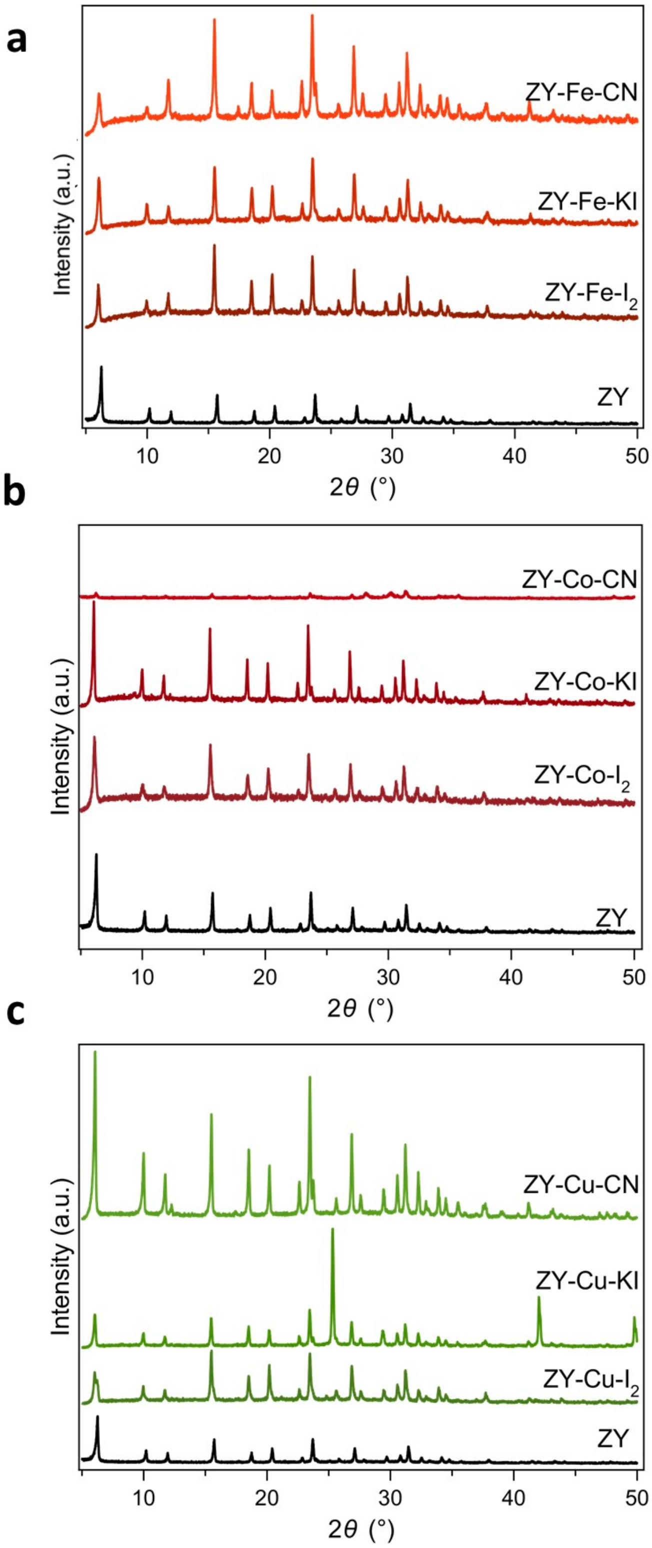

Fig. S1 PXRD patterns of the samples obtained from the **a** systems containing Fe, **b** systems containing Co and **c** systems containing Cu.

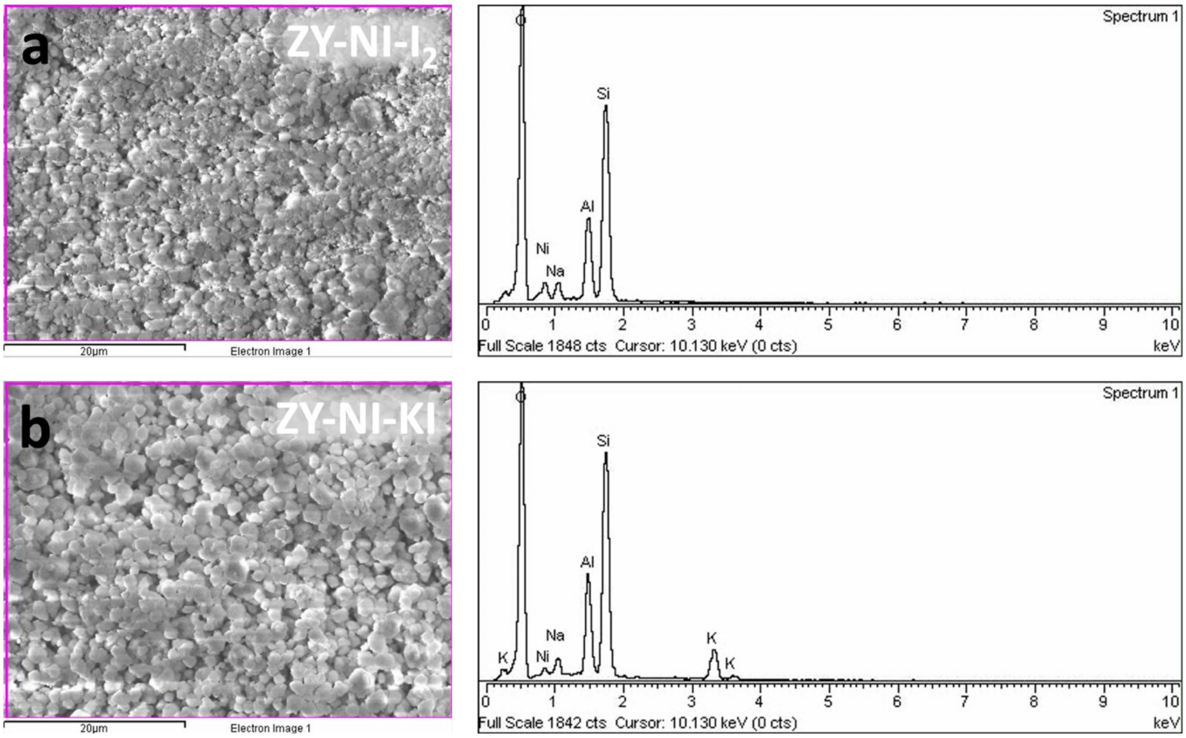

Fig. S2 EDS spectra of the samples ZY-Ni-I_2 and ZY-Ni-KI.

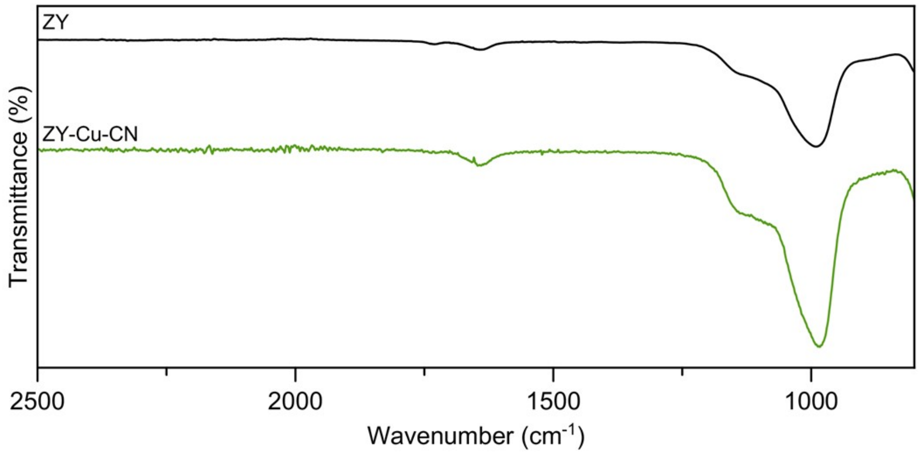

Fig. S3 Mid-IR spectrum of the sample obtained by milling ZY-Cu and KCN.

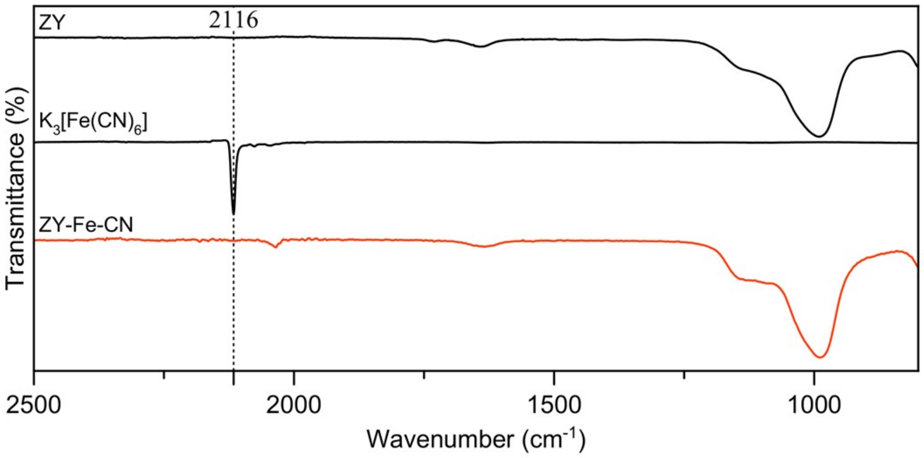

Fig. S4 Mid-IR spectrum of the sample obtained by milling ZY-Fe and KCN compared to a reference $K_3[Fe(CN)_6]$ sample.

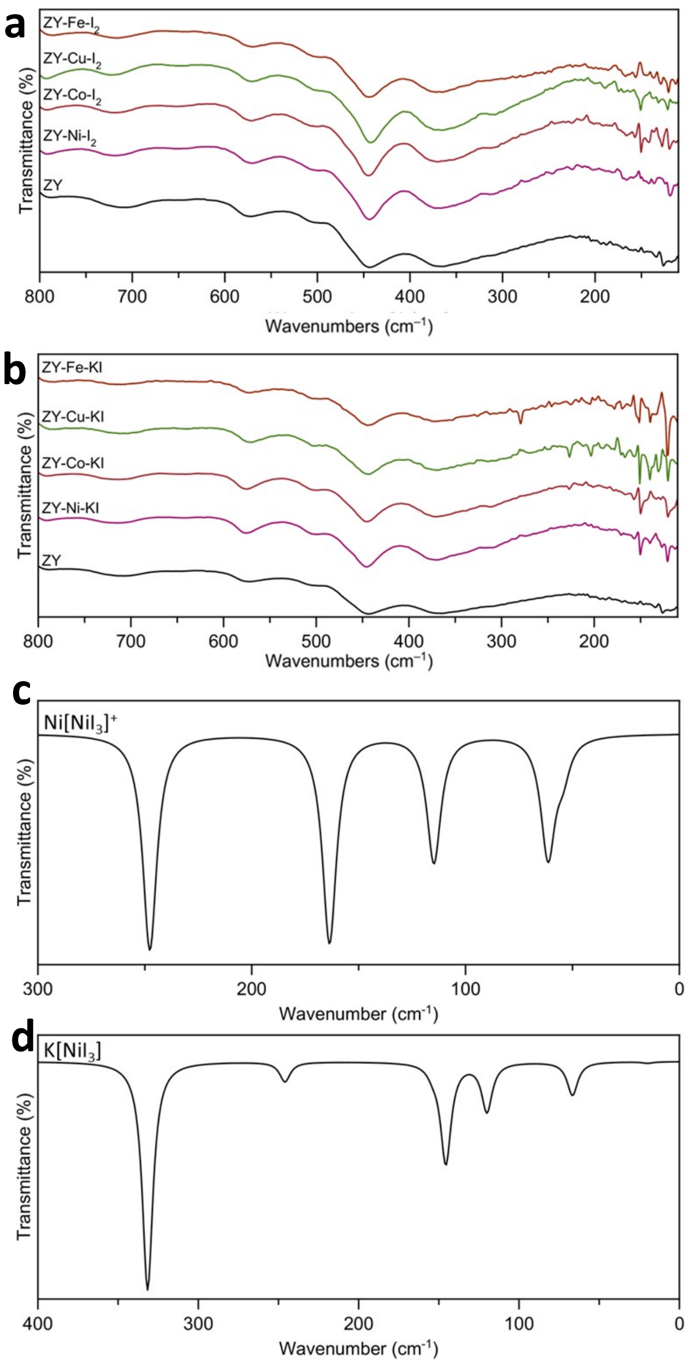

Fig. S5 Far-IR spectra of the samples obtained by milling ZY-M (M=Fe,Co,Ni,Cu) with halides, **a** systems containing I_2, **b** systems containing KI, **c** computed far-IR spectrum of $Ni[NiI_3]^+$, **d** computed far-IR spectrum of $K[NiI_3]$.

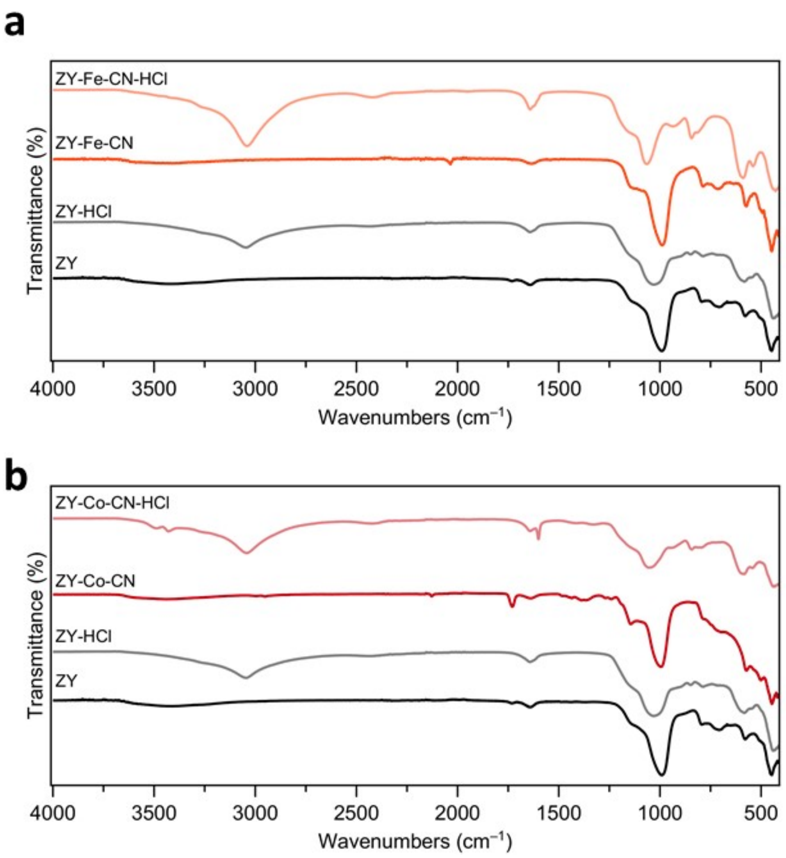

Fig. S6 Mid-IR spectra of the obtained samples exposed to gaseous HCl for 1 hour, **a** systems containing Fe, **b** systems containing Co.

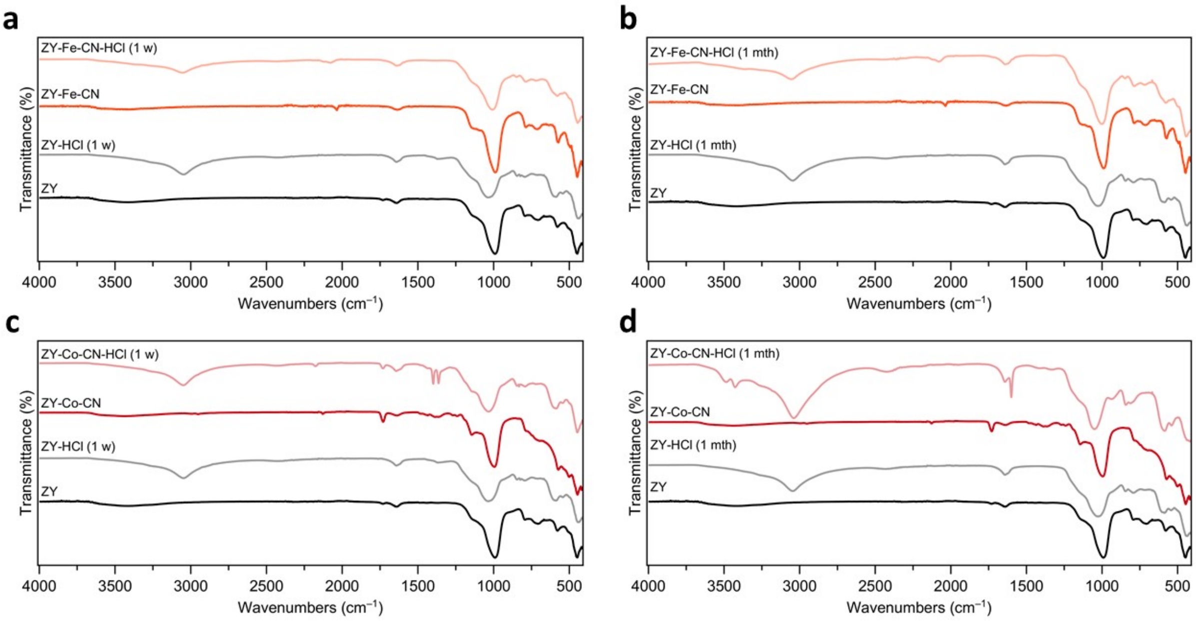

Fig. S7 Mid-IR spectra of the obtained samples exposed to gaseous HCl for one hour, **a** systems containing Fe measured 1 week upon the exposure, **b** systems containing Fe measured 1 month upon the exposure, **c** systems containing Co measured 1 week upon the exposure, **d** systems containing Co measured 1 month upon the exposure.

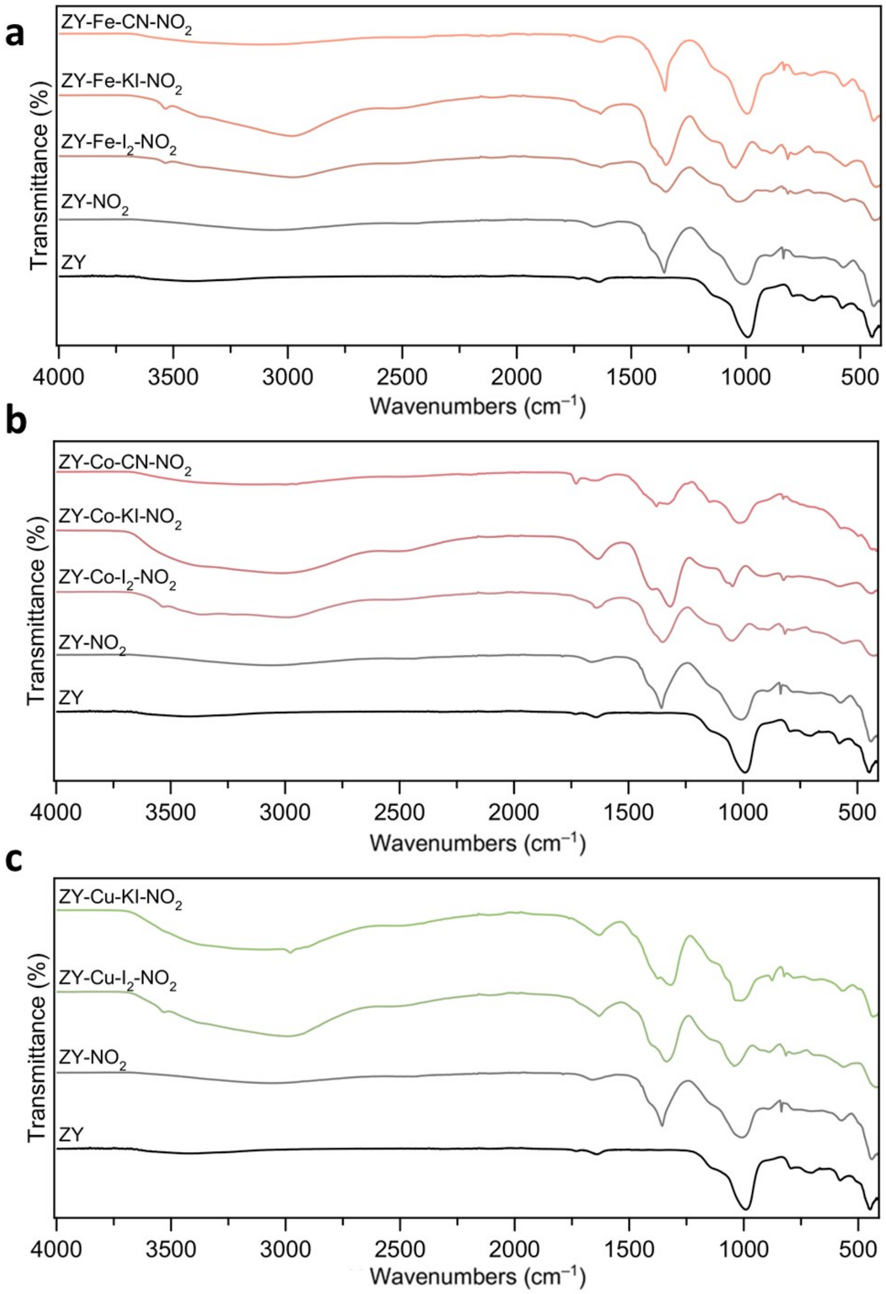

Fig. S8 Mid-IR spectra of the obtained samples exposed to gaseous NO_2 for 1 hour, **a** systems containing Fe, **b** systems containing Co, **c** systems containing Cu.

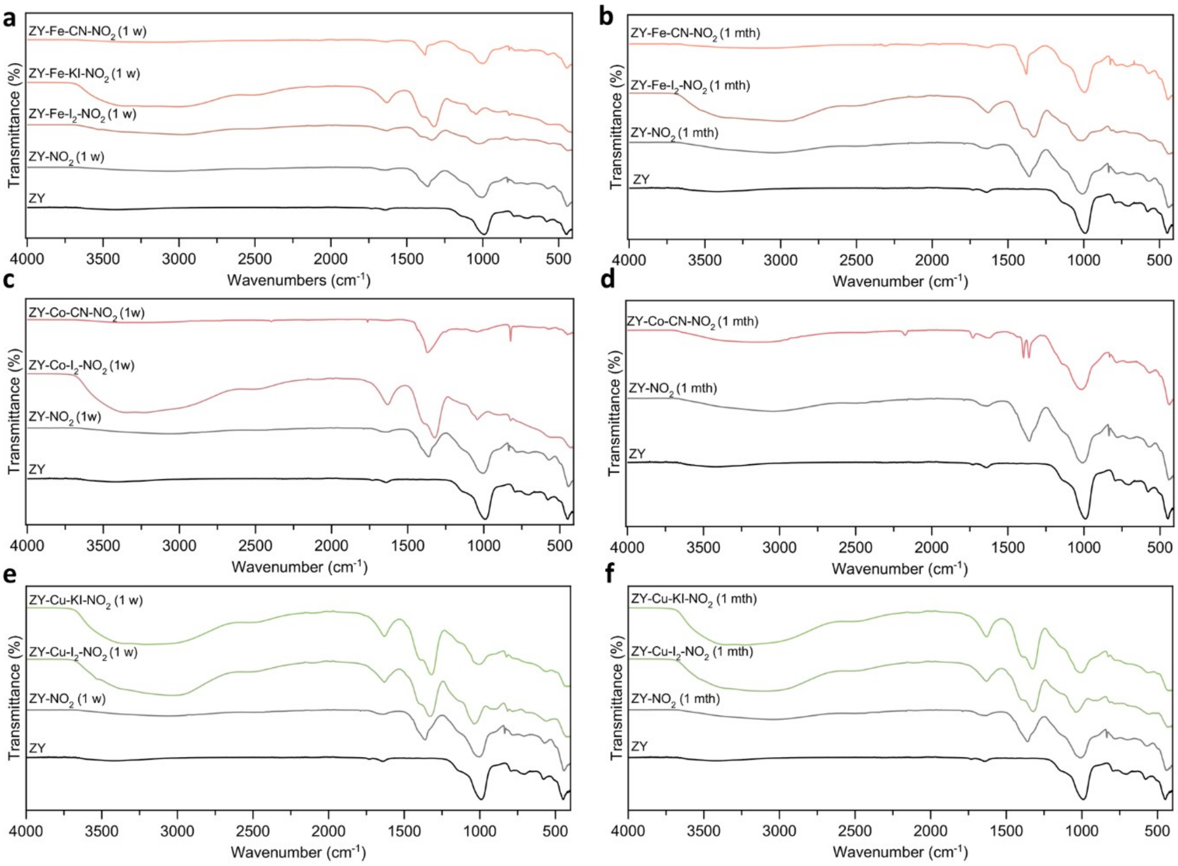

Fig. S9 Mid-IR spectra of the obtained samples exposed to gaseous NO_2 for one hour, **a** systems containing Fe measured 1 week upon the exposure, **b** systems containing Fe measured 1 month upon the exposure, **c** systems containing Co measured 1 week upon the exposure, **d** systems containing Co measured 1 month upon the exposure, **e** systems containing Cu measured 1 week upon the exposure, **f** systems containing Cu measured 1 month upon the exposure.

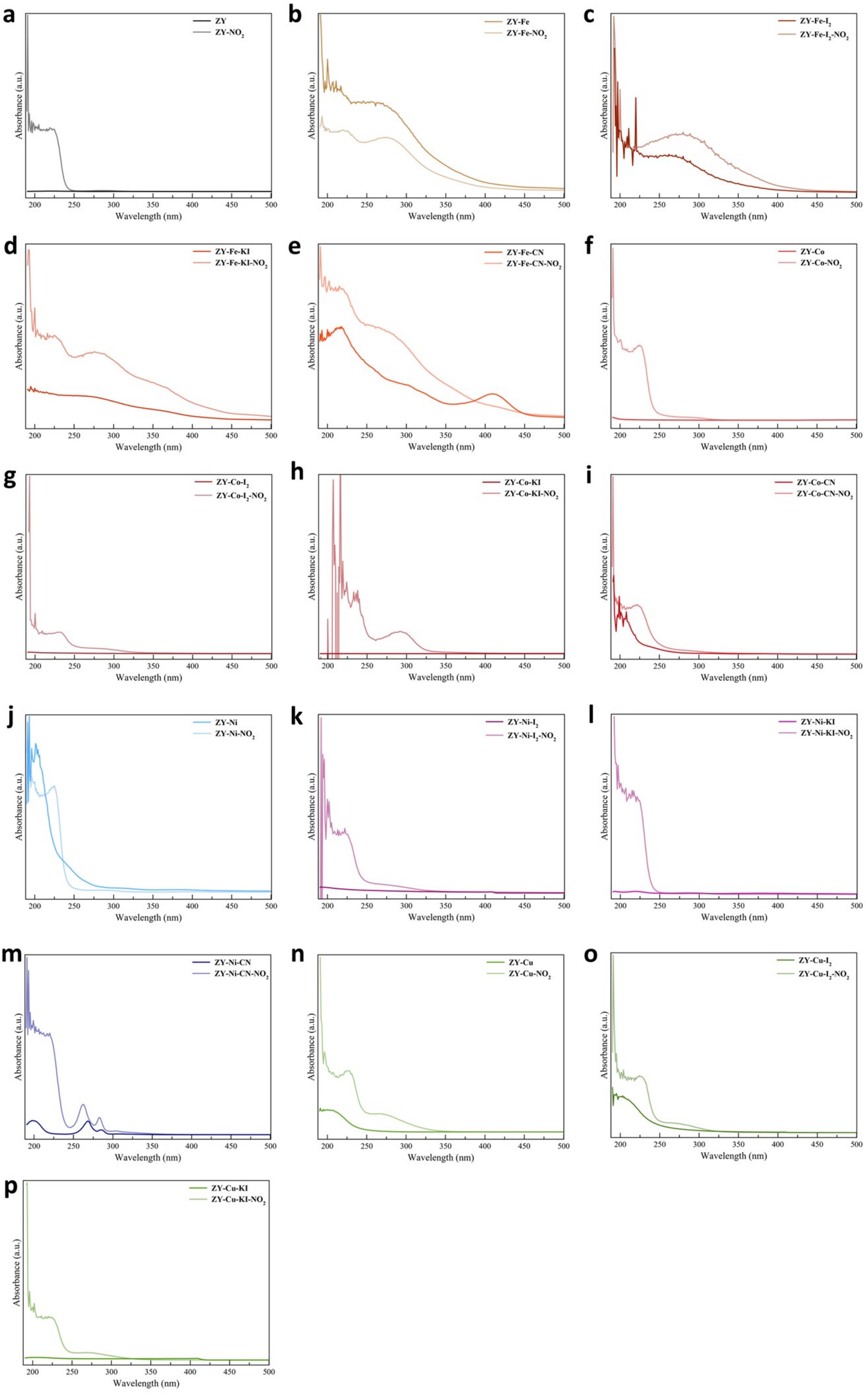
a
ZY
ZY-NO$_2$
b
ZY-Fe
ZY-Fe-NO$_2$
c
ZY-Fe-I$_2$
ZY-Fe-I$_2$-NO$_2$
d
ZY-Fe-KI
ZY-Fe-KI-NO$_2$
e
ZY-Fe-CN
ZY-Fe-CN-NO$_2$
f
ZY-Co
ZY-Co-NO$_2$
g
ZY-Co-I$_2$
ZY-Co-I$_2$-NO$_2$
h
ZY-Co-KI
ZY-Co-KI-NO$_2$
i
ZY-Co-CN
ZY-Co-CN-NO$_2$
j
ZY-Ni
ZY-Ni-NO$_2$
k
ZY-Ni-I$_2$
ZY-Ni-I$_2$-NO$_2$
l
ZY-Ni-KI
ZY-Ni-KI-NO$_2$
m
ZY-Ni-CN
ZY-Ni-CN-NO$_2$
n
ZY-Cu
ZY-Cu-NO$_2$
o
ZY-Cu-I$_2$
ZY-Cu-I$_2$-NO$_2$
p
ZY-Cu-KI
ZY-Cu-KI-NO$_2$
Absorbance (a.u.)
Wavelength (nm)
200
250
300
350
400
450
500

Fig. S10 Solid-state UV-Vis spectra of the samples prior to and after exposure to gaseous NO_2 for 1 h. **a**, unmodified zeolite Y. **b**-**e**, zeolite Y modified with Fe and I_2/KI/KCN. **f-i**, zeolite Y modified with Co and I_2/KI/KCN. **j-m**, zeolite Y modified with Ni and I_2/KI/CN. **n-p**, zeolite Y modified with Cu and I_2/KI/KCN.

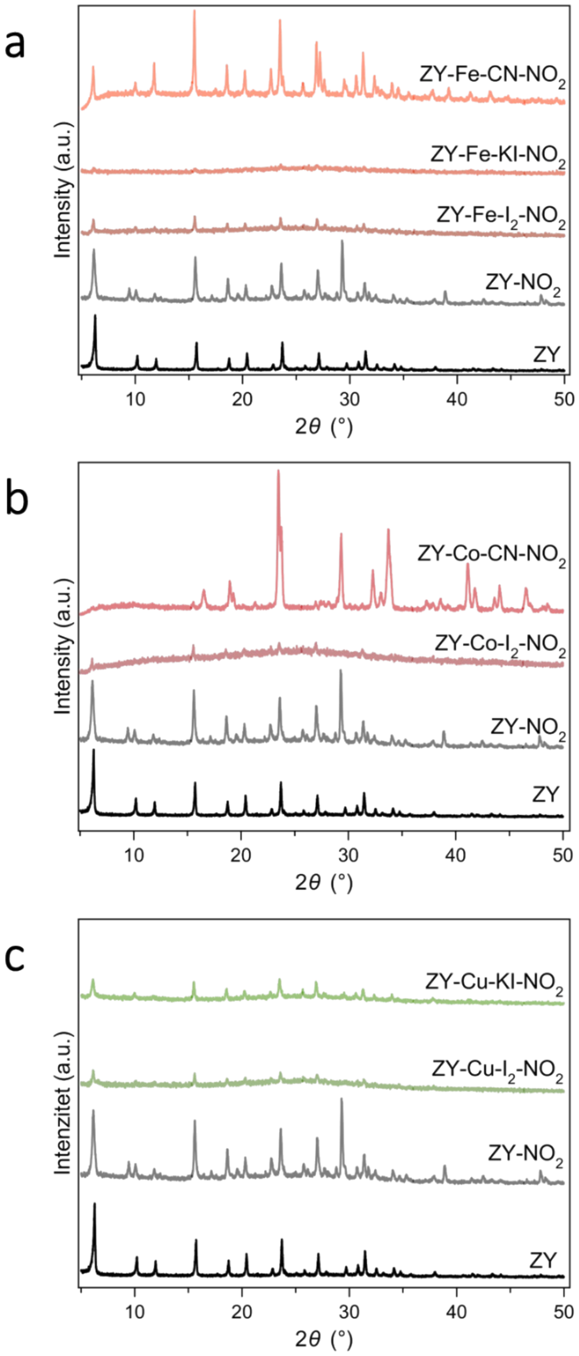

Fig. S11 PXRD patterns of the obtained samples exposed to gaseous NO_2 for 1 hour, **a** systems containing Fe, **b** systems containing Co, **c** systems containing Cu.

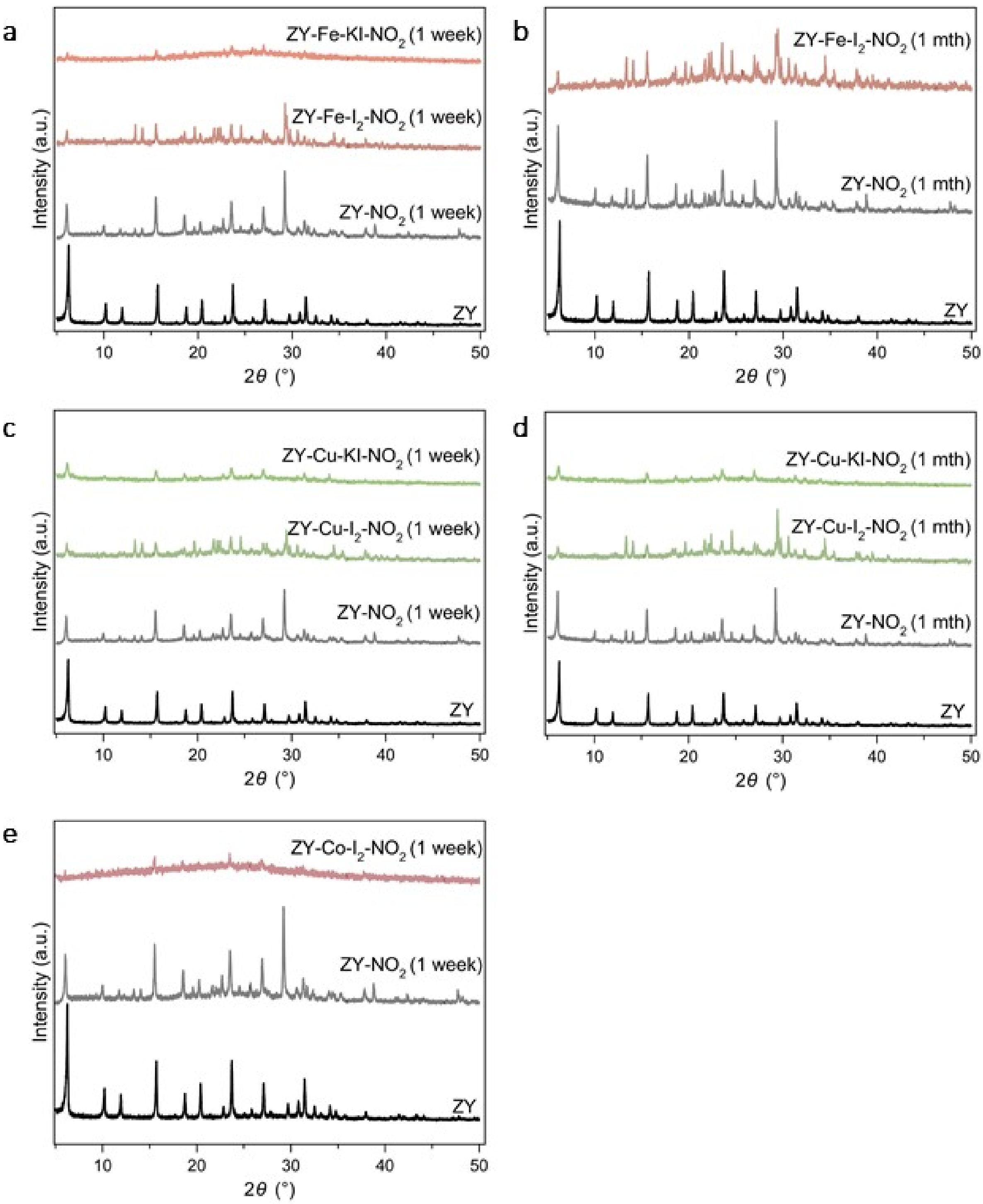

Fig. S12 PXRD patterns of the obtained samples exposed to gaseous NO_2 for one hour, **a** systems containing Fe measured 1 week upon the exposure, **b** systems containing Fe measured 1 month upon the exposure, **c** systems containing Cu measured 1 week upon the exposure, **d** systems containing Cu measured 1 month upon the exposure, **e** systems containing Co measured 1 week upon the exposure.

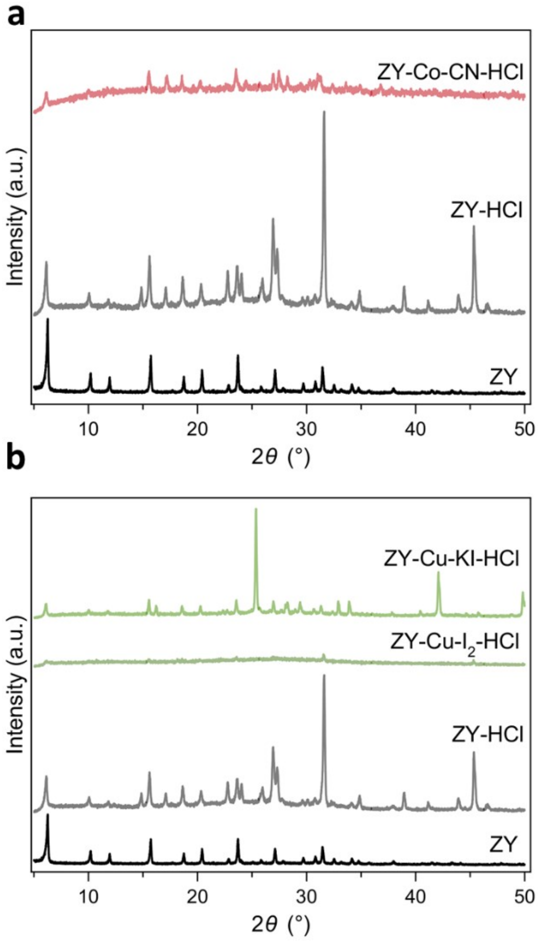

Fig. S13 PXRD patterns of the obtained samples exposed to gaseous HCl after 1 hour, **a** system containing Co, **b** systems containing Cu.

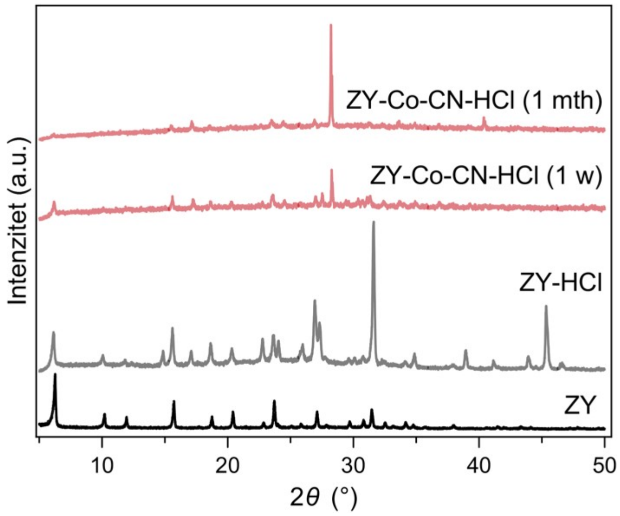

Fig. S14 PXRD patterns of the samples containing Co exposed to gaseous HCl for one hour measured 1 week and 1 month upon the exposure.

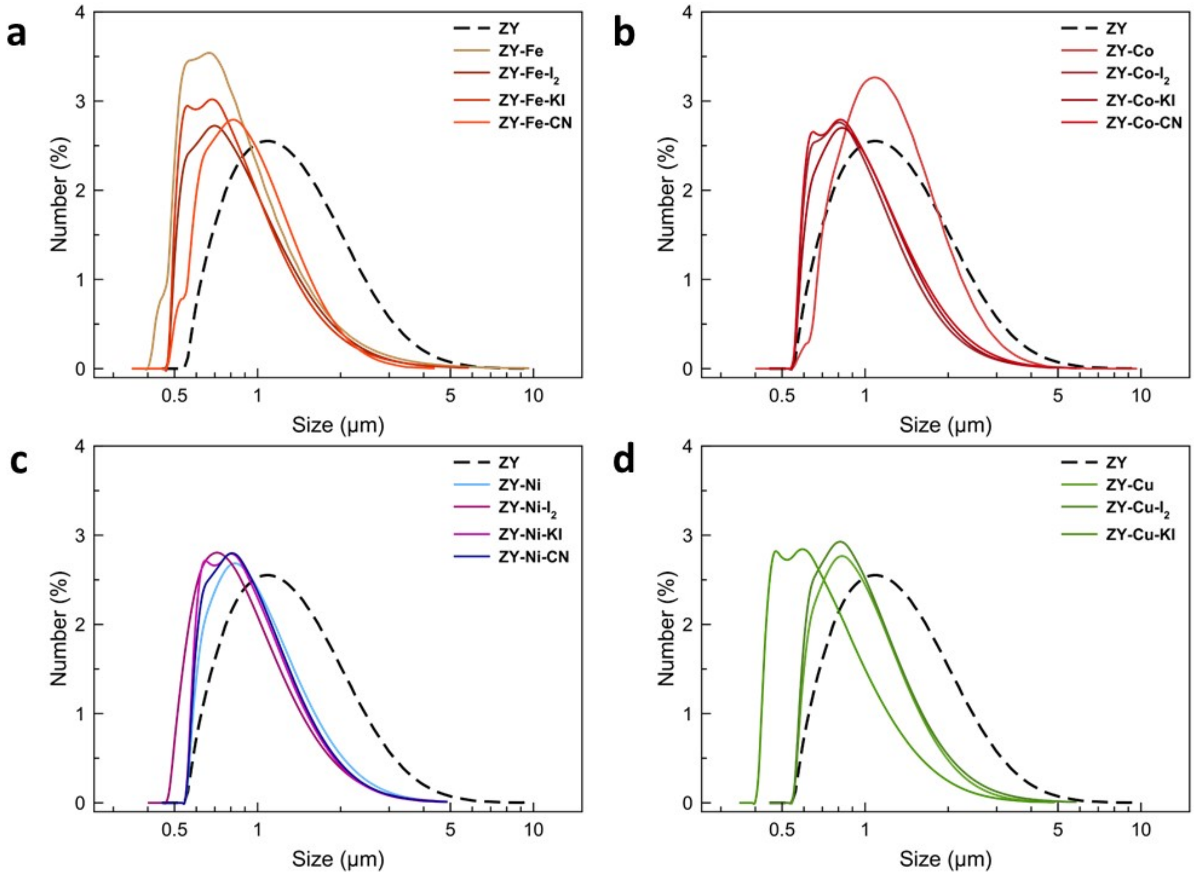

Fig. S15 Number PSD curves of the studied series of samples.

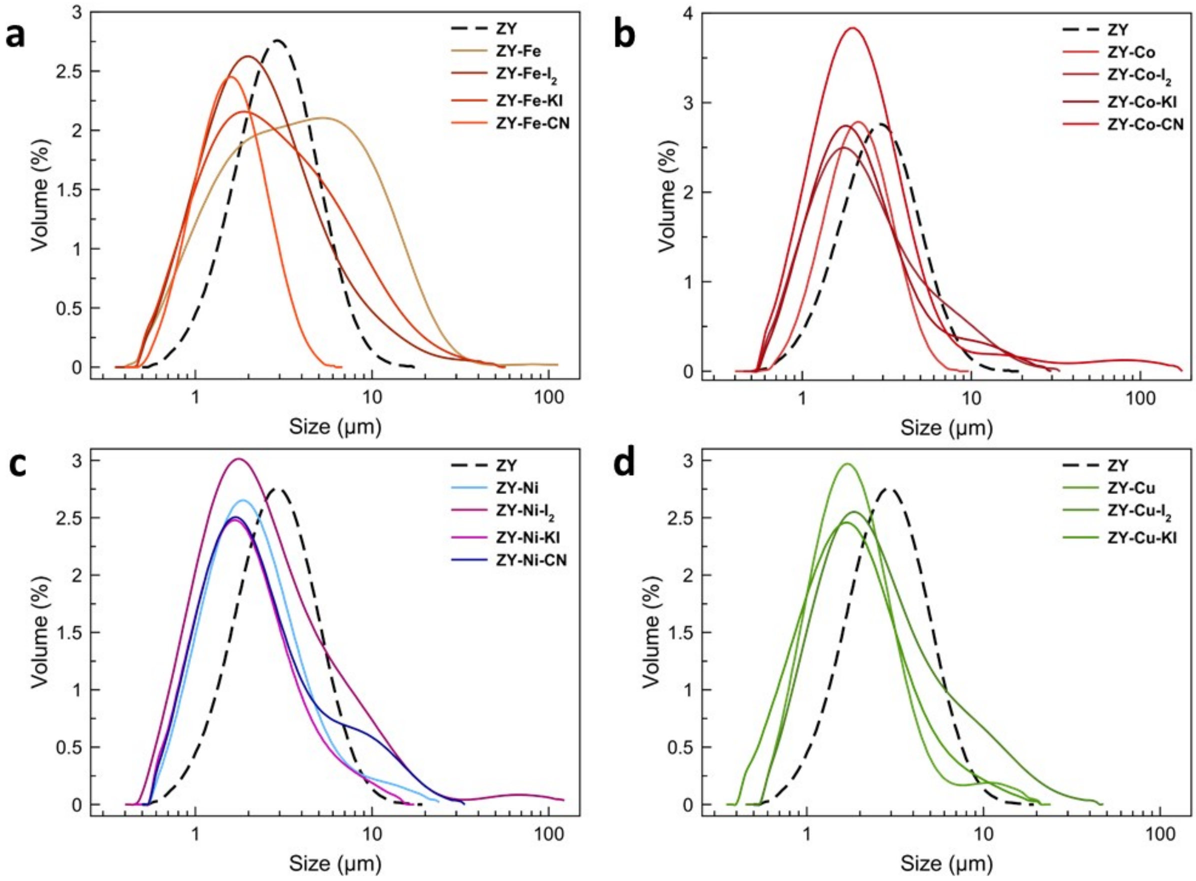

Fig. S16 Volume PSD curves of the studied series of samples.