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Direct accessibility of Mixed-Metal (III/II) Acid Sites through the Green, Scalable and Rational Synthesis of Porous Metal Carboxylates

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Experimental procedure

Mixed- metal building block synthesis

Fe/Ni and Fe/Co acetate mixed-metal building blocks were prepared using synthetic conditions adapted from literature[1] i.e. 1 g (4 mmol) of iron (III) acetate ($(Fe_3O(CH_3COO)_6.(H_2O)_3).ClO_4.2H_2O)_2$ was mixed with 2 g (8 mmol) of nickel (II) acetate tetrahydrate ($Ni(CH_3CO_2)_2.4H_2O$; 98+% from Alfa Aesar) or 2 g (8 mmol) cobalt (II) acetate tetrahydrate ($Co(CH_3CO_2)_2.4H_2O$; 98% from Alfa Aesar) in 20 mL of distilled water. The mixture was stirred at ambient temperature for 15 min and the resulting precipitated compound was obtained by filtration.

Fe/Mg acetate mixed-metal building block was synthesized as follow: 1 g (4 mmol) of iron (III) acetate was mixed with 0.85 g (4 mmol) of magnesium acetate tetrahydrate ($Mg(CH_3CO_2)_2.4H_2O$; 99% from Aldrich) in 30 mL absolute ethanol. The mixture was then heated to about 313 K and stirred for 15 min. After cooling, the obtained precipitated solid was recovered by filtration. It should be noted that the Fe/Mg molar ratio indicates an excess of magnesium, this due to the low ethanol solubility of the magnesium acetate tetrahydrate starting material (see EDX section below).

MIL-127 synthesis

Ligand synthesis: 3,3',5,5'-azobenzenetetracarboxylic acid ligand ($TazbH_4$) was prepared using known synthetic procedures.[3]

- MIL-127 (Fe) synthesis: The material was prepared following mild conditions reported recently.[4]

  MIL-127 (Fe) activation: Distilled water was added to the solid and the solution stirred for 1 hour and filtered off. Finally, 500 mL of absolute ethanol was added to the solid and the mixture refluxed for 1 hour and recovered via filtration and air dried. MIL-127 (Fe) is formulated as $Fe_3O(C_{12}N_2H_6(CO_2)_4)_{3/2}X.(H_2O)_2$.(solvent) (X= Cl, OH); about 15 % of the mass of the product corresponds to solvent molecules (see TGA below) i.e. ethanol and water. About 2.2g of product was recovered (79 % yield based on metal)

- MIL-127 (Fe, Ni) synthesis: 3.4 mL isopropanol and 0.6 mL distilled water were added to 0.37 g (1 mmol) $TazbH_4$ and 0.39 g (0.68 mmol) of Fe/Ni acetate building block. After about 3 days of reflux, the solid was recovered via filtration.

- MIL-127 (Fe, Co) synthesis: 3.4 mL isopropanol and 0.6 mL distilled water were added to 0.37 g (1 mmol) $TazbH_4$ and 0.39 g (0.68 mmol) of Fe/Co acetate building block. After about 3 days of reflux, the solid was recovered via filtration.

- MIL-127 (Fe, Mg) synthesis: 8 mL Isopropanol were added to 0.73 g (2 mmol) $TazbH_4$ and 0.73 g (1.35 mmol) of Fe/Mg acetate building block. After about 3 days of reflux, the solid was recovered via filtration.

  MIL-127 mixed-metal activation: The as-synthesized compounds were firstly washed with distilled water in order to remove un-reacted mixed metal acetates by suspending the product in distilled water under magnetic stirring at ambient temperature for 1 hour. The compounds were recovered by filtration, washed with ethanol, and dried under vacuum. Subsequently, the compounds were washed with ethanol to remove free acid by suspending the solid in ethanol and stirring under reflux for 4 hours. The compounds were then collected by filtration. The compounds are formulated as: $Fe_2MO(C_{12}N_2H_6(CO_2)_4)_{3/2}.(H_2O)_3$.(solvent) (M= Ni, Co or Mg)

MIL-100 (Fe, Ni) synthesis:

The mixed metal Fe/Ni acetate building block (90 mg, 0.15 mmol) and 1,3,5-benzenetricarboxylic acid H_3BTC (69.5 mg, 0.35 mmol) were dispersed in 4 ml N'N'-dimethylformamide (DMF). After the addition of the solvent, the mixture was heated in a hydrothermal bomb to 438 K for 48 hours. Activation was carried out by refluxing the samples in water for about 20 hours, filtering and then leaving to dry at room temperature. MIL-100 is formulated as: $Fe_2NiO(C_6H_3(CO_2)_3)_2.(H_2O)_3$.(solvent)

MIL-88B(Fe, Ni) synthesis:

The mixed metal Fe/Ni acetate building block (45 mg, 0.08 mmol) and 1,3,5-benzenedicarboxylic acid H_3BDC (42 mg, 0.76 mmol) were added to 1.5 mL DMF and 5 mL toluene. The mixture was then heated in a hydrothermal bomb to 423 K for 18 h. The as-synthesized compound (closed form) was filtrated and washed with water. Part of the solid was then heated to 423 K for 3h to confirm the material is flexible. MIL-88B (Fe,Ni) is formulated as: $Fe_2NiO(C_6H_4(CO_2)_2)_3.(H_2O)_3$.(solvent). The as-synthesize form was used to calculate the cell parameters.

X-Ray Powder Diffraction

Data was collected on a Bruker D8 Advance diffractometer (CuKα1 radiation (λ = 1.540598 Å) with a Debye-Scherrer geometry and a D5000 Siemens diffractometer (CuKα1,2 radiation (λ = 1.540598 Å). The D8 system is equipped with a LynxEye detector. Indexing and pattern matching were performed using Topas software.[5]

- **Mixed-metal building blocks**

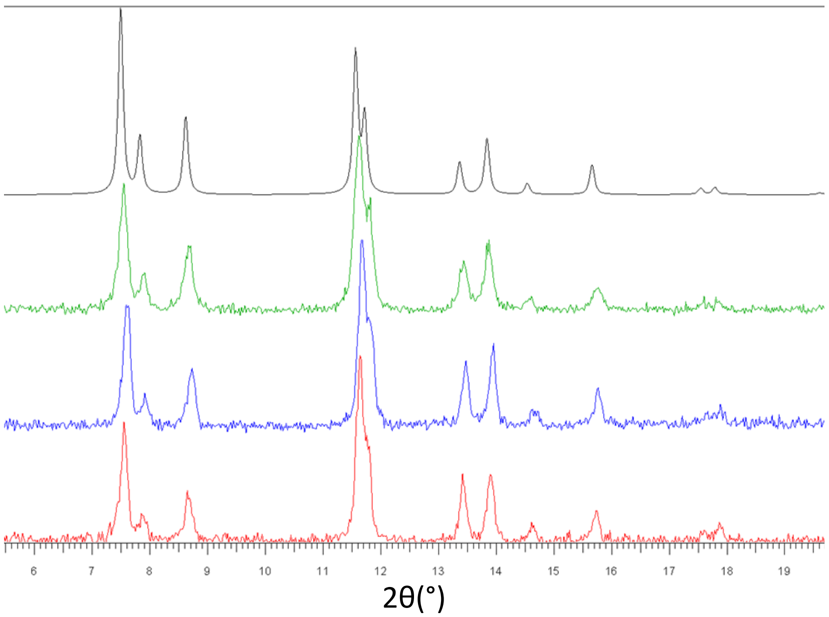

Figure S1: X-ray powder diffraction for the Iron/Nickel acetate, Iron/Cobalt acetate, Iron/Magnesium acetate building block in red, blue and green respectively compared to calculated pattern (in black) from Iron/Nickel acetate data[1]

- **MIL-127**

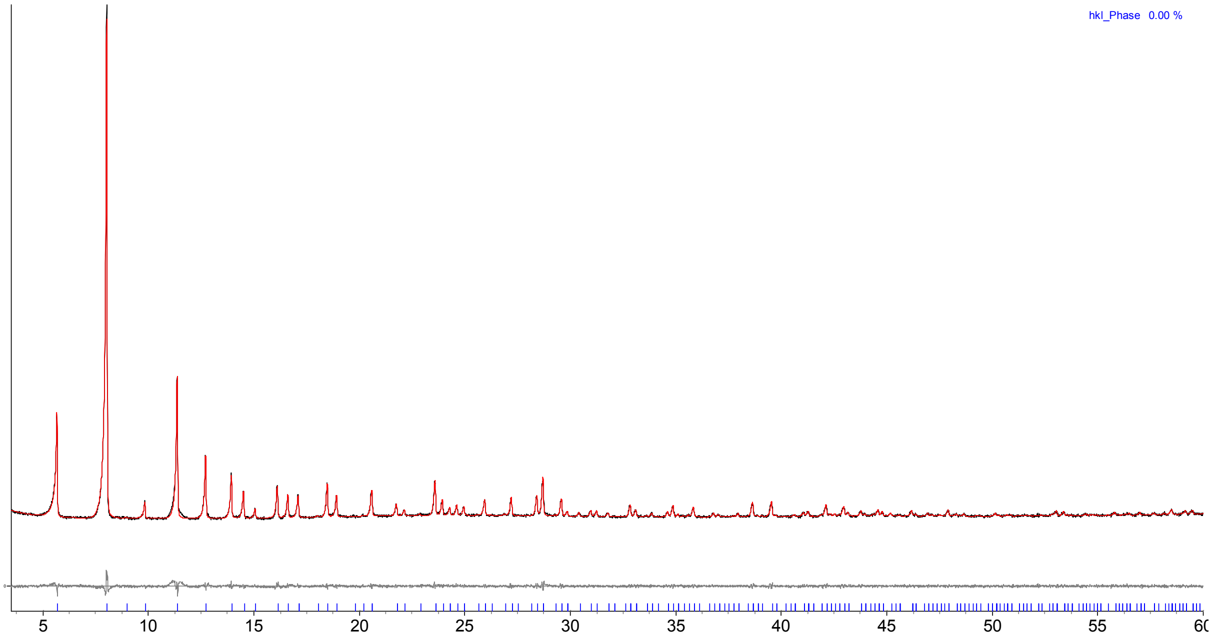

Figure S2: Pattern matching for MIL-127(Fe), a = 21.94(5) (cubic), space group: P-43n (Rwp=1.26).

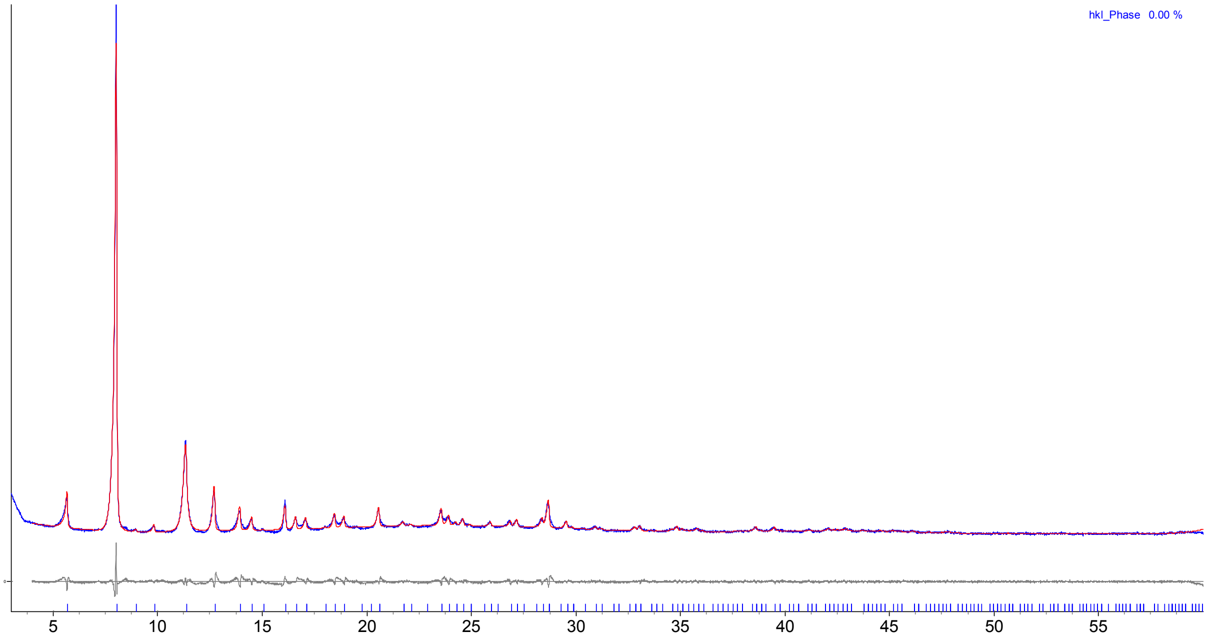

Figure S3: Pattern matching for MIL-127(Fe, Ni), a = 21.947(3) (cubic), space group: P-43n (Rwp=2.97).

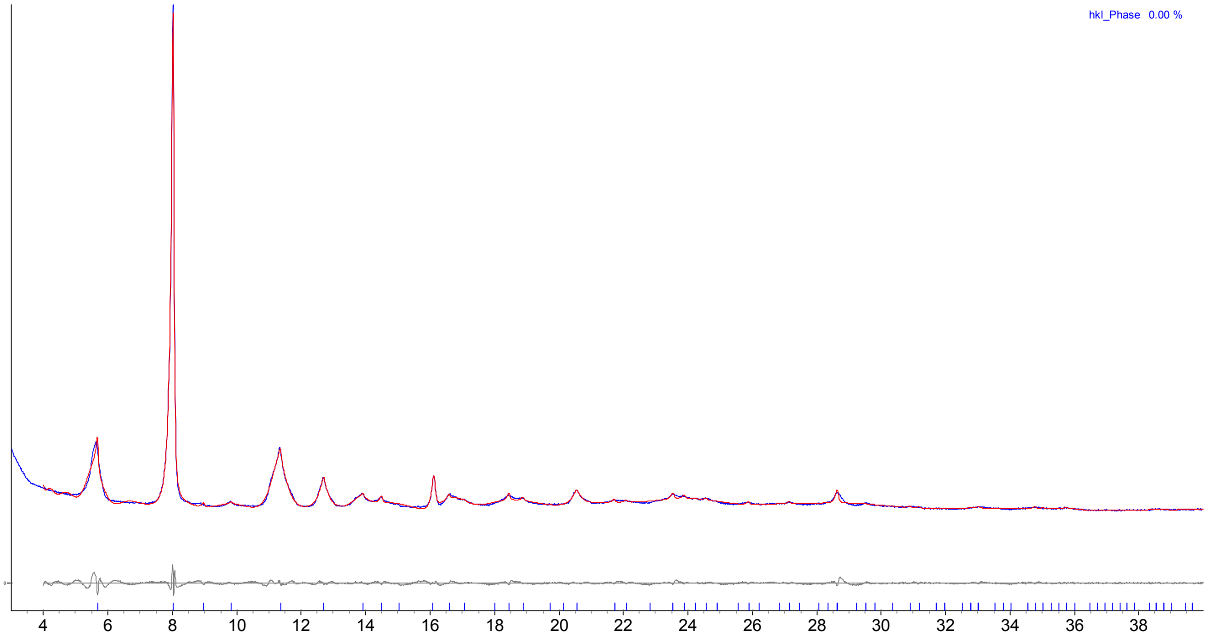

Figure S4: Pattern matching for MIL-127(Fe, Mg), a = 21.988(2) (cubic), space group: P-43n (Rwp=1.36).

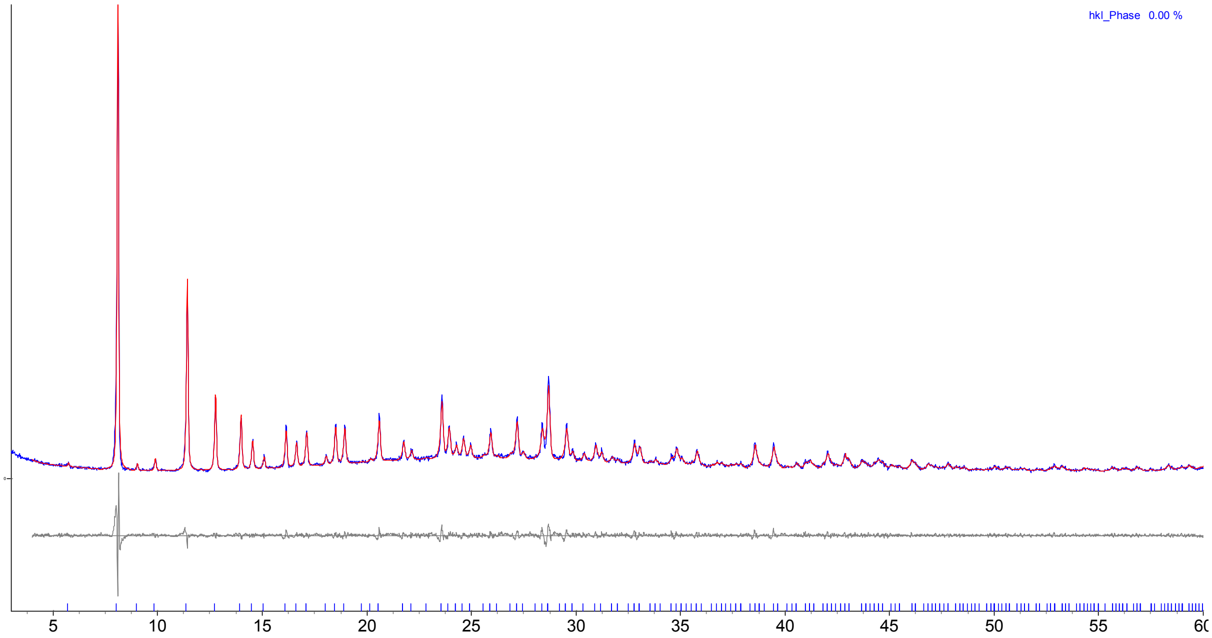

Figure S5: Pattern matching for MIL-127(Fe, Co), a = 21.039(2) (cubic), space group: P-43n (Rwp=6.58).

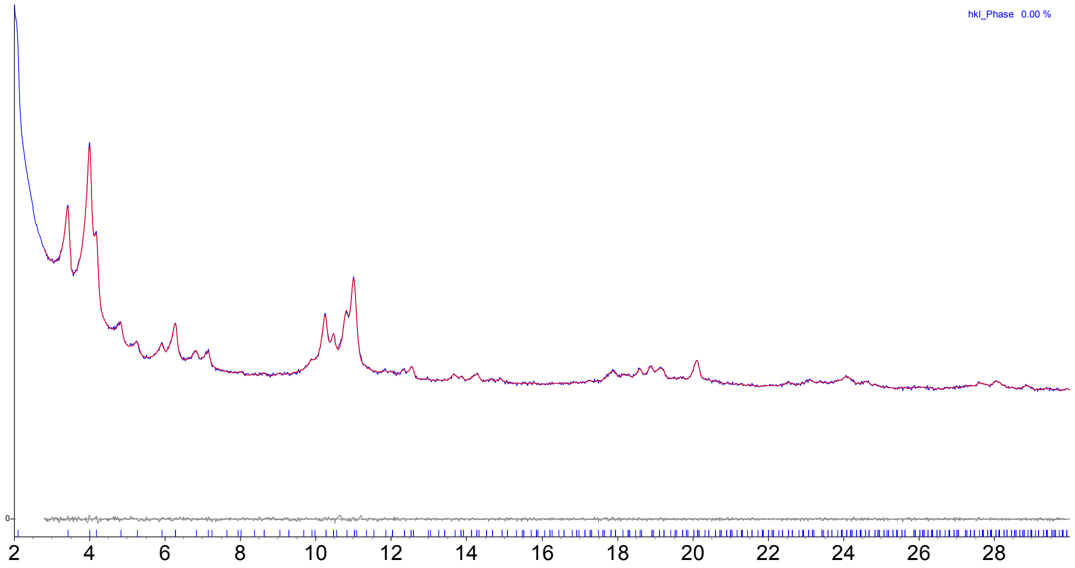

Figure S6: Pattern matching for MIL-100(Fe, Ni), a = 73.08(5) (cubic), space group: Fd-3m (Rwp=0.646)

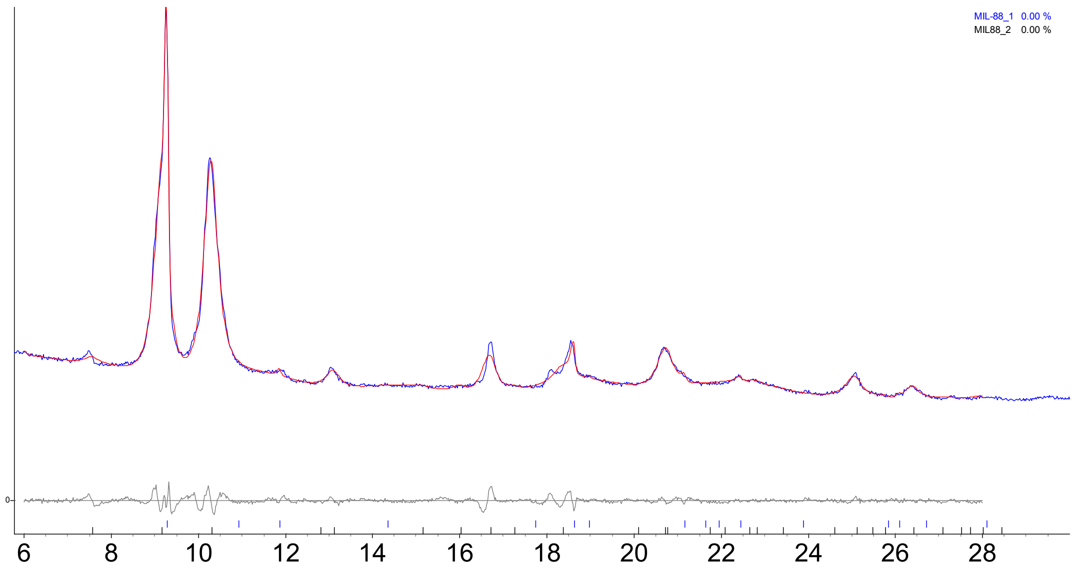

Figure S7: Pattern matching for MIL-88B (Fe, Ni), major form: a = 13.481(8), c = 17.135(9) (hexagonal), space group: P62c. Secondary form: a = 9.342(7), c = 19.04(1) (Rwp=2.016)

Energy-Dispersive X-Ray spectroscopy (EDX)

The Iron/Nickel, Iron/Cobalt and Iron/Magnesium ratio was evaluated using a Jeol JSM-7001F microscope using gold coated samples equipped with an energy-dispersive X-ray (EDX) spectrometer with a X-Max SDD (Silicon Drift Detector) by Oxford. Some of the data was taken using a Jeol JSM-5800LV Scanning Microscope equipped with an integrated EDX system.

- Acetate building blocks

<u>Fe/Ni acetate</u>:

	1	2	3	4	*Average*
Fe (mol%)	68.9	68.8	69.1	69.1	*68.9*
Ni (mol%)	31.1	31.2	30.9	30.9	*31.1*

<u>Fe/Co acetate</u>:

	1	2	3	*Average*
Fe (mol%)	67.0	67.7	68.4	*67.7*
Co (mol%)	33	32.3	31.6	*32.3*

<u>Fe/Mg acetate</u>:

	1	2	3	*Average*
Fe (mol%)	55.9	50.3	62.5	*56.2*
*Mg (mol%)	44.1	49.7	37.5	*43.8*

- Mixed-metal MIL-127

MIL-127 (Fe, Ni):

	1	2	3	*Average*
Fe (mol%)	65.6	67.2	65.4	*66.1*
Ni (mol%)	34.4	32.8	34.6	*33.9*

MIL-127 (Fe, Co):

	1	2	3	*Average*
Fe (mol%)	67.0	67.7	68.4	*67.7*
Co (mol%)	33.0	32.3	31.6	*32.3*

MIL-127 (Fe, Mg):

	1	2	3	*Average*
Fe (mol%)	69.3	62.8	65.8	*66.0*
*Mg (mol%)	30.7	37.2	34.2	*34.0*

- Mixed-metal MIL-100±

	1	2	3	*Average*
Fe (mol%)	79.1	80.1	81.7	*80.3*
Ni (mol%)	20.9	19.9	18.3	*19.7*

- Mixed-metal MIL-88B

	1	2	3	*Average*
Fe (mol%)	66.6	68.6	69.9	*68.4*
Ni (mol%)	33.4	31.4	30.1	*31.6*

*Due to the low alcohol solubility of Mg acetate, an excess of Mg is observed.
±The excess of iron is due to iron oxide impurities present in mixture with MIL-100(Fe, Ni)

Infra-red Spectroscopy

Transmission IR spectra were recorded in the 500-4000 cm^{-1} range, with 4 cm^{-1} resolution on a Nicolet Nexus spectrometer.

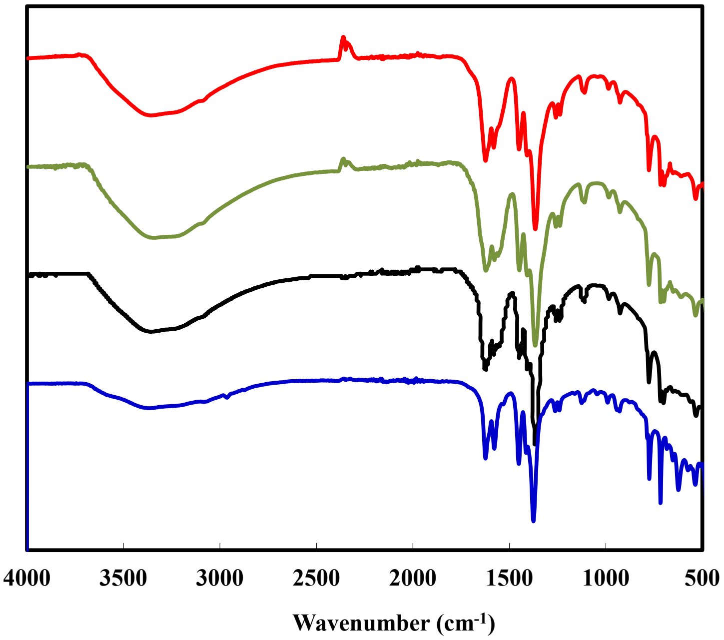

Figure S8: IR spectra for activated MIL-127(Fe), MIL-127(Fe, Co), MIL-127(Fe, Mg) and MIL-127(Fe, Ni) in blue, red, green and black respectively. Only traces of free acid are present.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were performed by a PerkinElmer STA 6000 apparatus. The measurement was conducted under O_2 with a heating rate of 3°C.min^{-1}. The weigh losses are in good agreement with the expected range: about 71% ligand loss for MIL-127(Fe, Mg) (72% calc.), about 70% ligand loss for MIL-127(Fe, NI) (69% calc.), about 67% ligand loss for MIL-127(Fe, Co) (69% calc.) and about 68% ligand loss for MIL-127(Fe) (69% calc.)

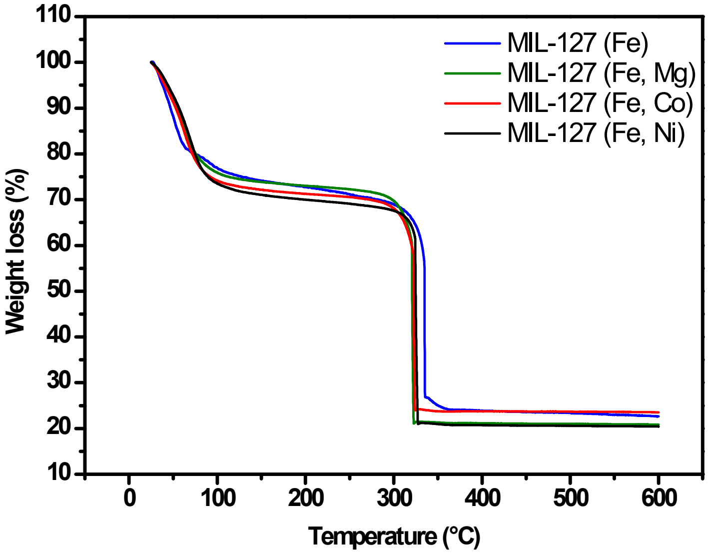

Figure S9: Thermogravimetric analysis for the MIL-127(Fe), MIL-127(Fe, Mg), MIL-127(Fe, Co) and MIL-127(Fe, Ni).

Nitrogen Sorption

N_2 adsorption/desorption analysis was performed on a BelsorpII mini BEL apparatus. The samples were degassed at 473 K for 3 hours. The obtained accessible surface areas are: 1370 $m^2 \cdot g^{-1}$ for MIL-127(Fe, Co), 1370 $m^2 \cdot g^{-1}$ for MIL-127(Fe, Mg), 1450 $m^2 \cdot g^{-1}$ for MIL-127(Fe, Ni) and 1300 $m^2 \cdot g^{-1}$ for MIL-127(Fe) (calculated using the BET model).

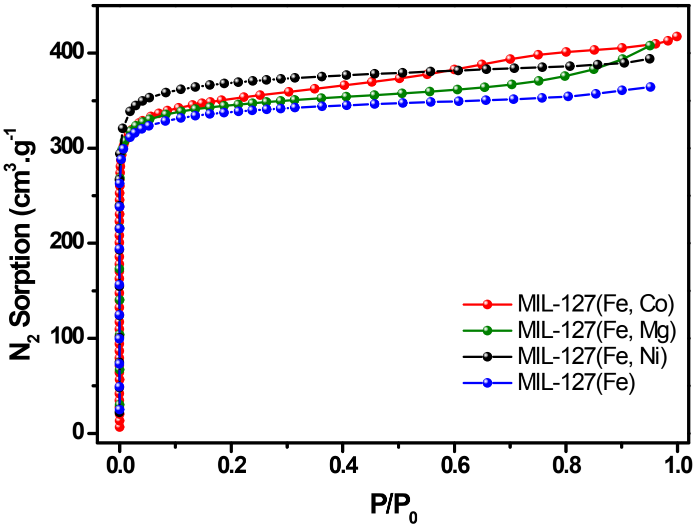

Figure S10: Nitrogen sorption isotherm for the MIL-127(Fe, Co), MIL-127(Fe, Mg), MIL-127(Fe, Ni) and MIL-127(Fe) in red, green, black and blue respectively.

In-situ infra red spectroscopy

In order to characterize qualitatively and quantitatively the physicochemical properties of the samples, an adsorption of probe molecules followed by infrared spectroscopy was performed.

Solid samples were analyzed as self-supported wafers (ca. 15 mg). The wafers were finally placed in an IR quartz cell equipped with KBr windows. The cell was connected to a vacuum line for evacuation, calcinations and introduction of known doses of vapours. The compounds were activated under secondary vacuum (10^{-3} Pa) from room temperature (ca. 293 K) to either 423 or 503 K. Transmission spectra were recorded in the 500 – 5600 cm^{-1} range at 4 cm^{-1} resolution on a Nicolet 6700 FTIR spectrometer equipped with an extended KBr beam splitting device and a DTGS detector.

For both activation temperatures, adsorption of NO revealed a band at 1797 cm^{-1}, similar to that recorded for MIL-127(Fe)[6], and a band at 1874 cm^{-1}. These bands are assigned to NO chimisorbed respectively to Fe^{2+} and Ni^{2+} species. Their band areas allow determining the concentration of Ni^{2+} and Fe^{2+} sites.

The areas of the bands of NO adsorbed on Fe^{2+} and Ni^{2+} were determined for various NO pressures at the two calcination temperatures 423 and 503 K (Figures S11 and S12). They lead to the molar absorption coefficient ε of each band and thus the number of Fe^{2+} and Ni^{2+} sites. The first NO doses only interacted with Fe^{2+}. This allowed the determination of the corresponding absorption coefficient (Figure S12A). For higher loadings, NO adsorbed both on Fe^{2+} and Ni^{2+} sites. For the calculation of the absorption coefficient of NO--- Ni^{2+}, the amount of NO interacting with Fe^{2+} was thus subtracted from the total amount introduced.

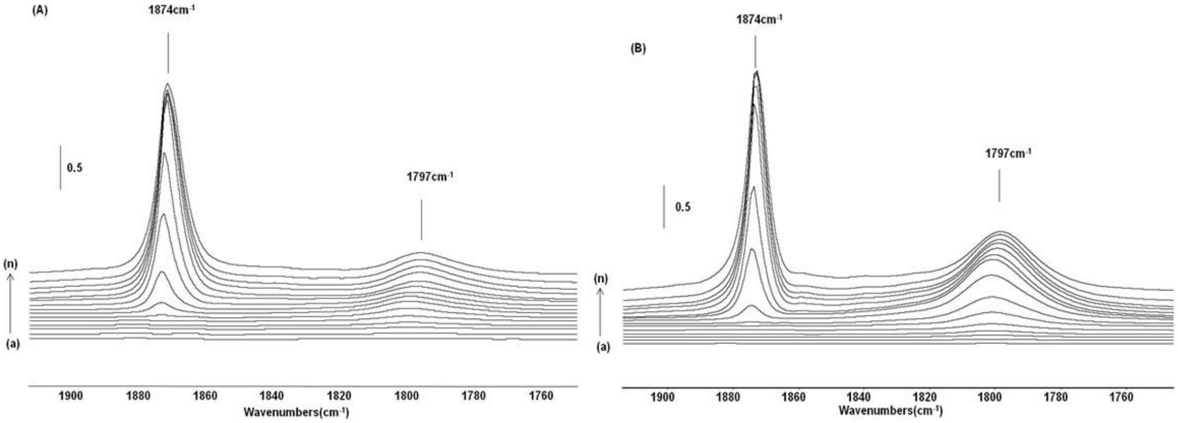

Figure S11. Infrared spectra of MIL-127 (Fe, Ni) after introduction of increasing pressures of NO: 50, 115, 180, 330, 660, 1330, 2735, 5490, 8220, 15180, 22060, 32205, 42750 Pa (a-m respectively), followed finally by the introduction of an equilibrium pressure of NO equal to 665 Pa (n).

(A) Spectra after activation of the solid at 423 K; (B) Spectra after activation of the solid at 503 K.

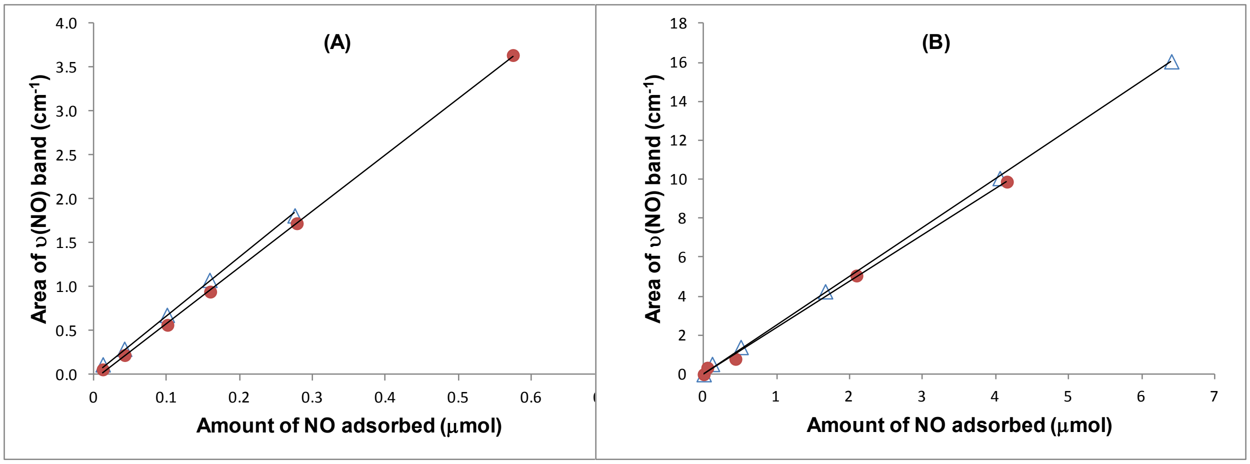

Figure S12. Area of the IR bands of NO adsorbed on (A) Fe^{2+} and (B) Ni^{2+} vs. the amount of NO specifically adsorbed on the corresponding site. (❒) Solid activated at 423 K ; (●) Solid activated at 503 K.

After activation at 423 K, the absorption coefficient ε was equal to 5.0 $cm.\mu mol^{-1}$ for the band of NO adsorbed on Ni^{2+} at 1874 cm^{-1} while it was equal to 13.4 $cm.\mu mol^{-1}$ for the band at 1797 cm^{-1} (NO adsorbed on Fe^{2+}). Similar measurements at 503 K lead to absorption coefficients respectively equal to 4.8 and 12.6 $cm.\mu mol^{-1}$. Average values can thus be taken for the absorption coefficients of NO adsorbed on Ni^{2+} (4.9 $cm.\mu mol^{-1}$) and on Fe^{2+} (13 $cm.\mu mol^{-1}$).

Therefore, after activation at 423 K, the number of sites at saturation can be calculated and is equal to about 800 $\mu mol.g^{-1}$ for Ni^{2+} sites and 67 $\mu mol.g^{-1}$ for Fe^{2+} sites. On the sample activated at 503 K, the amount of Ni^{2+} (band at 1874 cm^{-1}) was equal to about 600 $\mu mol.g^{-1}$ while the number of Fe^{2+} (band at 1797 cm^{-1}) was equal to 212 $\mu mol.g^{-1}$.

^{57}Fe Mössbauer Spectrometry

^{57}Fe Mössbauer measurements were performed at 300K and 77K in a transmission geometry using a conventional constant acceleration transmission spectrometer with a ^{57}Co(Rh) source and a bath cryostat. The spectrometer was previously calibrated using a standard foil while the isomer shift values are quoted to that of α-Fe at 300K. The samples consist of powder of respective systems containing 5mg of Fe/cm^2. The hyperfine structures were systematically refined using the MOSFIT program by means of quadrupolar components composed of lorentzian lines.

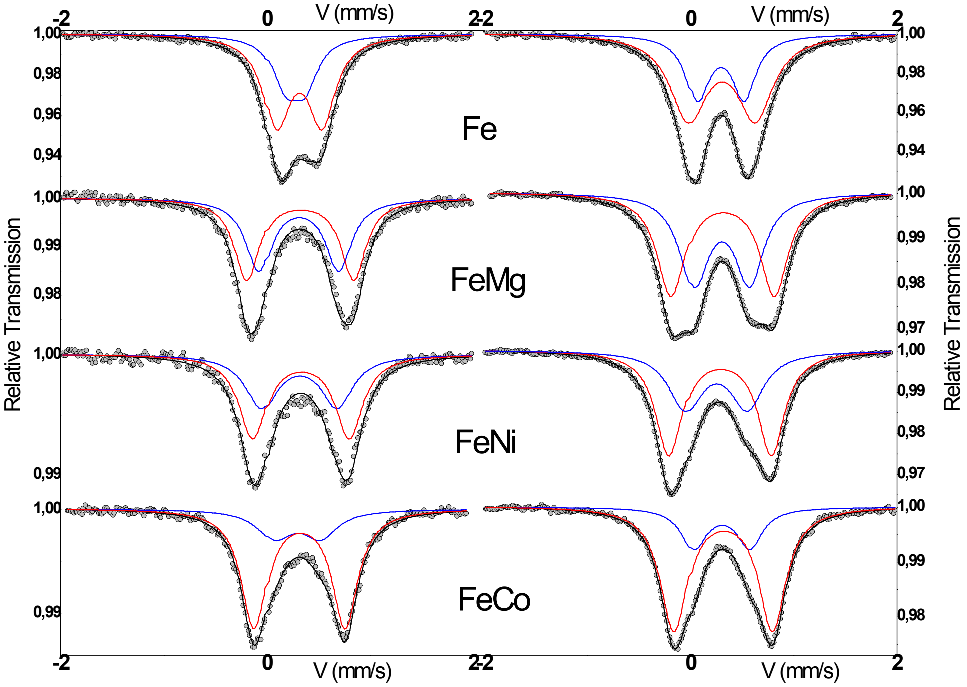

Figure S13: 300K transmission Mössbauer spectra for the MIL-127(Fe), MIL-127(Fe, Mg), MIL-127(Fe, Ni), MIL-127(Fe, Co) (left) and the corresponding acetate building blocks starting materials (right) (2 mm/s).

CO_2, CO Sorption

Adsorption microcalorimetry

Around 0.15 g of sample was used for adsorption experiments. Prior to each experiment, samples were outgassed ex situ at 473 K for 16 h under a secondary vacuum of 10^{-3} mbar.

The microcalorimetry experiments were performed using a home built manometric adsorption apparatus coupled with a Tian–Calvet type microcalorimeter.[7] This experimental device allows the determination of the adsorption isotherm and the adsorption enthalpy simultaneously using a point by point introduction of gas to the sample. A multi-pneumovalve system allows the introduction of the adsorbate to the sample. An exothermic thermal effect accompanied each introduction. This peak in the curve of energy with time has to be integrated to provide an integral (or pseudo-differential) molar enthalpy of adsorption for each dose. Experiments were carried out at 303 K and up to 20 bars. However, most differences in the data are visible up to 2 bars.

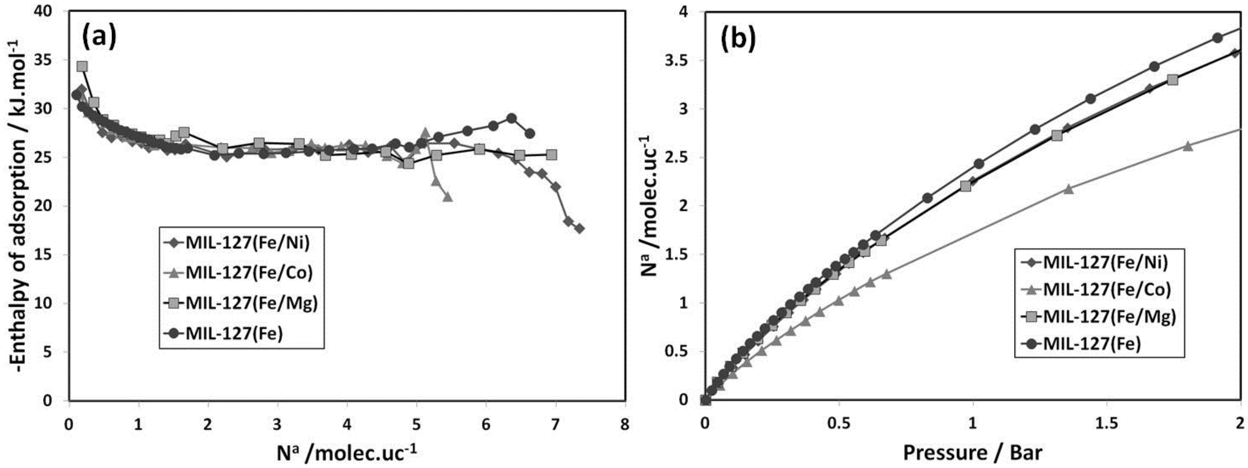

Figure S14 : Differential enthalpies of adsorption (a) and adsorption isotherms (b) for carbon dioxide in MIL-127(Fe/X) at 303 K.

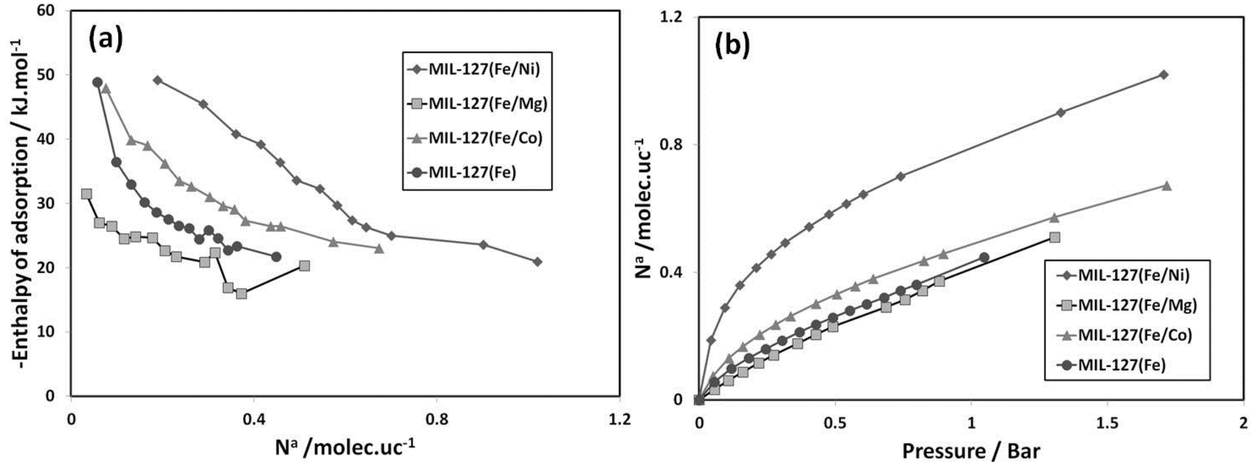

Figure S15 : Differential enthalpies of adsorption (a) and adsorption isotherms (b) for carbon monoxide in MIL-127(Fe/X) at 303 K.

Fig S15 shows the adsorption isotherms and the differential enthalpies of adsorption for carbon monoxide in MIL-127(Fe) and the three mixed metal samples MIL-127(Fe, X) at 303 K (with X = Ni, Co or Mg). The enthalpy of adsorption for the samples in the low pressure region is in the range -45 to -50 kJ.mol^{-1} except for MIL-127(Fe, Mg) sample which is around -31.5 kJ.mol^{-1}. The enthalpies of adsorption decrease with increasing loading to reach a plateau at approximately -20 kJ.mol^{-1}. This corresponds to a change in isotherm slope at low pressure (at 0.2 bars). These trends suggest that at low pressure, adsorption occurs on specific sites, which are probably here the unsaturated metals, prior to coverage of the remaining surface. It appears that the adsorption isotherms obtained with the MIL-127(Fe, Ni) shows the highest capacity for carbon monoxide adsorption. MIL-127(Fe, Co) capacity is lower than this sample, whilst the enthalpy of adsorption at low pressure is quite similar for these samples and for MIL-127(Fe). These greater performances for MIL-127(Fe, Ni) reflect its higher specific surface area (1460 m^2.g^{-1}) compared to the MIL-127(Fe, Co) sample (1290 m^2.g^{-1}). This result seems to be confirmed by the more rapid decrease in the enthalpy for the MIL-127(Fe, Co) with respect to the MIL-127(Fe, Ni), indicating that there are fewer metal sites for carbon monoxide in MIL-127(Fe, Co). The MIL-127(Fe, Mg) shows the lowest capacity to adsorb carbon monoxide in good agreement with its lower enthalpy of adsorption (-31.5 kJ.mol^{-1}) with respect to the other samples (-45 to -50 kJ.mol^{-1}). This suggests that the presence of Mg as an unsaturated metal leads to a decrease in the carbon monoxide adsorption strength and capacity.

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