Supplementary Information

Co-doping of MOF-5 framework and its effect on gas adsorption behaviour

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Contents

Experimental Section

(a) Powder X-Ray Diffraction (PXRD) patterns were obtained in a Philips XPERT PRO using CuKα (λ = 1,542 Å) radiation. In order to avoid the effects of preferred crystal orientation, obtained crystals were grounded and Mica sample was used as an internal standard to calculate the displacement error of the instrument.

(b) Diffuse-reflectance UV-Visible (DR-UV-Vis) spectra were recorded on a Varian CARY-500 spectrophotometer equipped with a diffuse reflectance accessory in the wavelength range 200-600 nm. A halon white reflectance standard was used as a reference material.

(c) Thermogravimetric analyses (TGA) were carried out in a flowing air atmosphere of 100 ml/min with a heating rate of 3 ºC/min up to 1000 ºC using a TA Instruments SDT 2860 apparatus.

(d) Inductively coupled plasma spectra (ICP) were recorded on a Varian VISTA AX equipment.

(e) Elemental chemical analyses for C, N, and H were carried out using a Vario EL III analyzer with temperatures in the oven and in the reduction coil of 1150 and 850 °C, respectively, and equipped with a thermal conductivity detector.

(f) Gas adsorption isotherms were obtained in a Hiden Analytical Intelligent Gravimetric Analyser equipped with an ultra high vacuum system. The microbalance showed a long-term stability of ± 1 μg with a weight resolution of 0.2 μg. The approach to equilibrium was measured in real time using a computer algorithm. The pressure was monitored by a transducer in an standard range of 0-10 bar. The buoyancy effects were corrected as a function of temperature taking into account the void volume of the cell determined with He gas at 77 K, and assuming that the amount of He adsorbed is negligible.
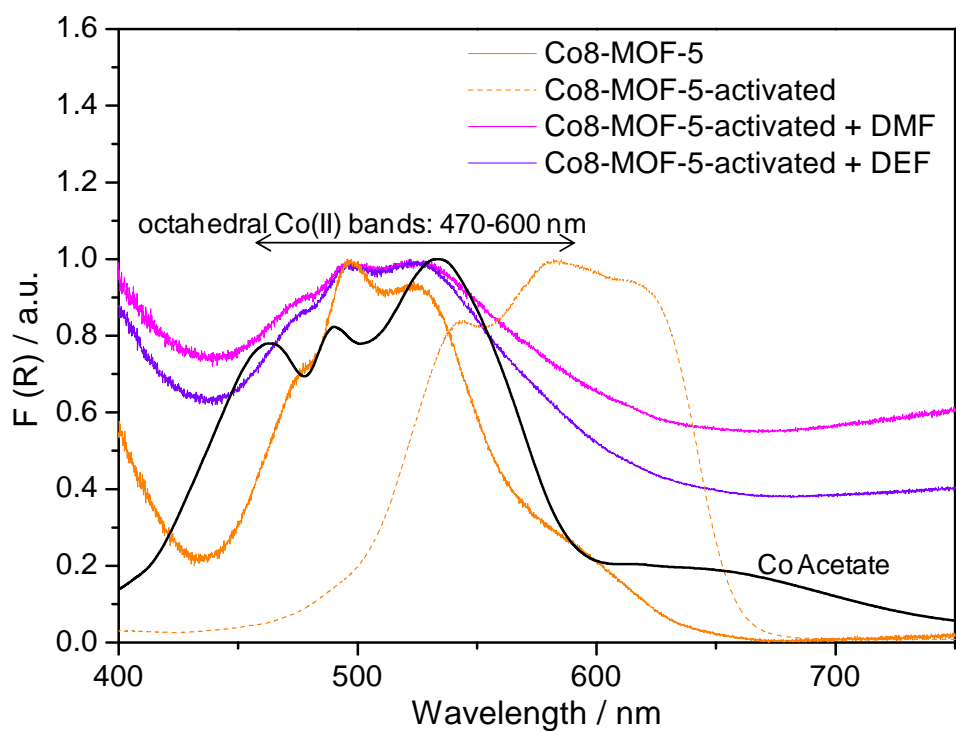
PXRD patterns
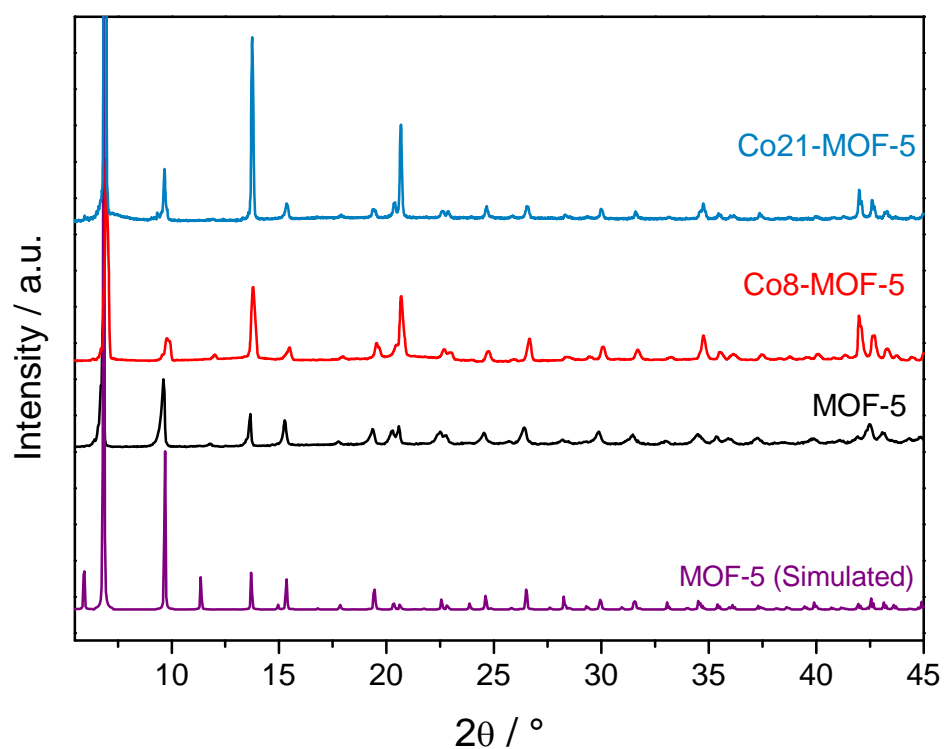
Figure S1. Comparison of the powder X-ray diffraction patterns recorded for a finely powdered bulk sample of the as-prepared Co8-MOF-5, Co21-MOF-5 and MOF-5 materials and the simulated MOF-5[1]. MOF-5 is the unique crystalline phase present in all samples.

(1) J. Rowsell, E. Spencer, J. Eckert, J. Howard, O.M. Yaghi, *Science*, 2005, **309**, 1350.

DR-UV-Vis spectra

Figure S2. Comparison of the DR-UV-Vis spectra of cobalt acetate and Co8-MOF-5 samples: as-prepared, activated, and activated with dimethylformamide and diethylformamide. Note that Co(II) tetrahedral coordination in activated Co8-MOF-5 turns to octahedral after solvent soak (dimethylformamide or diethylformamide), confirming the reversibility in Co coordination change with the presence/absence of solvent inside the cavities.

Hydrogen isotherms fit

Sips method[1] is applied to a Freundlich isotherm, and also to a new theoretical isotherm which reduces to the Freundlich type for small pressures, but exhibits saturation for large pressures. It is shown that this isotherm corresponds to a distribution function which differs very little from a Gaussian one. The case of atomic adsorption of gases is also considered.

$$\theta = \frac{n}{m} = \left(\frac{b \cdot p^s}{1 + b \cdot p^s} \right)$$
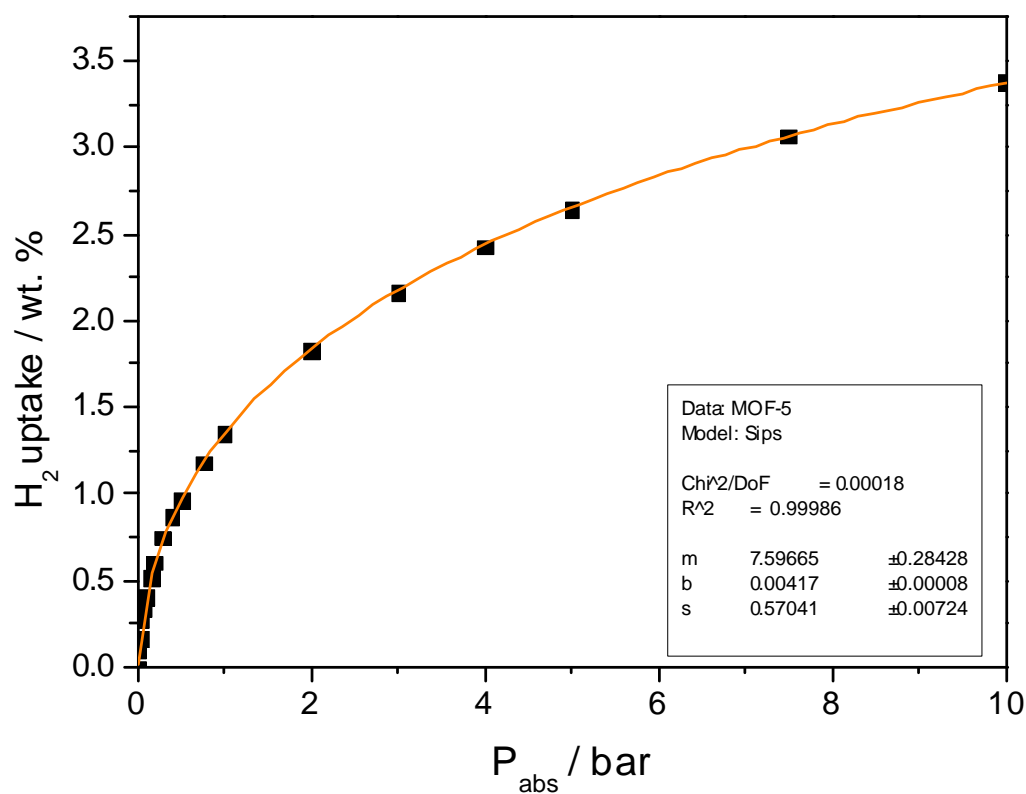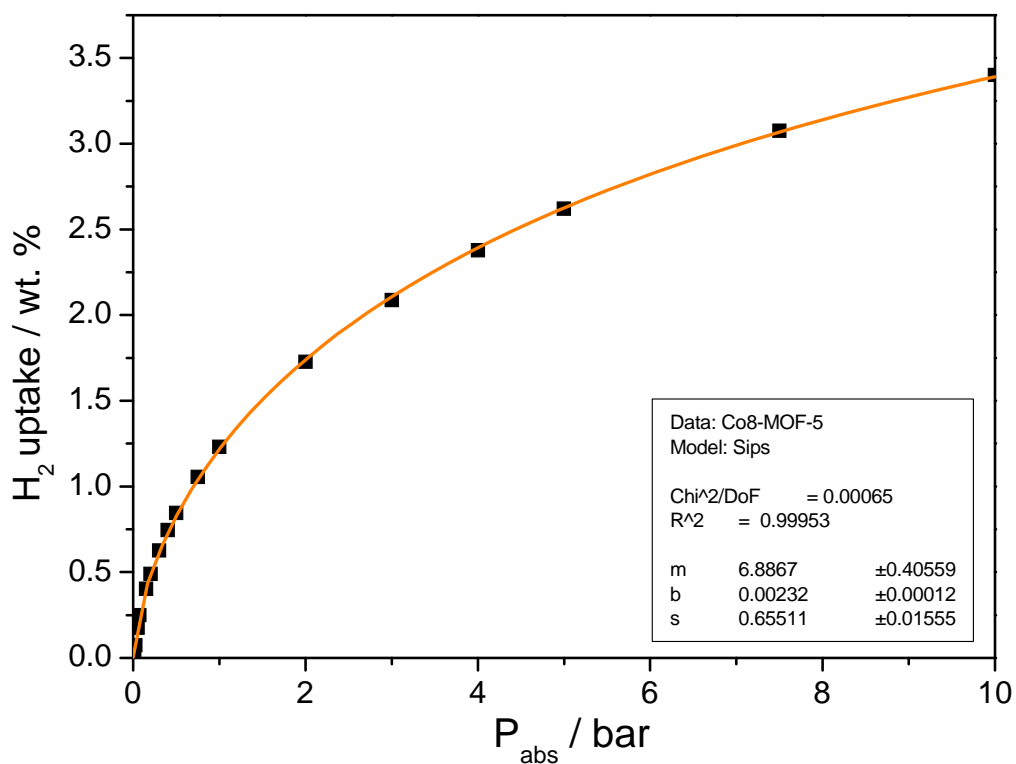
Where:
θ: coverage
n: gas adsorbed
m: gas adsorbed in saturation
b, s: parameters related to the interaction between adsorbate and surface.
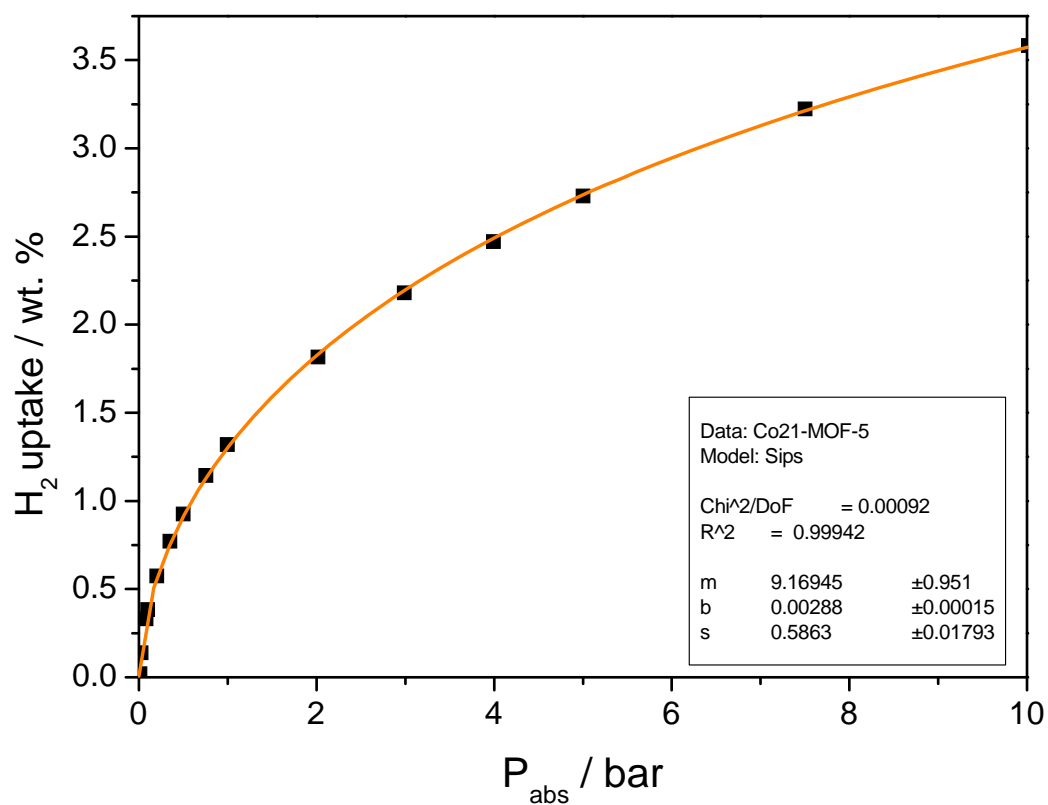

Figure S3A. Sips fit to H_2 adsorption isotherms at 77 K for sample MOF-5.

(1) R.J. Sips, *J. Chem. Phys.*, 1948, **16**, 490.

Figure S3B. Sips fit to H$_2$ adsorption isotherms at 77 K for sample Co8-MOF-5.
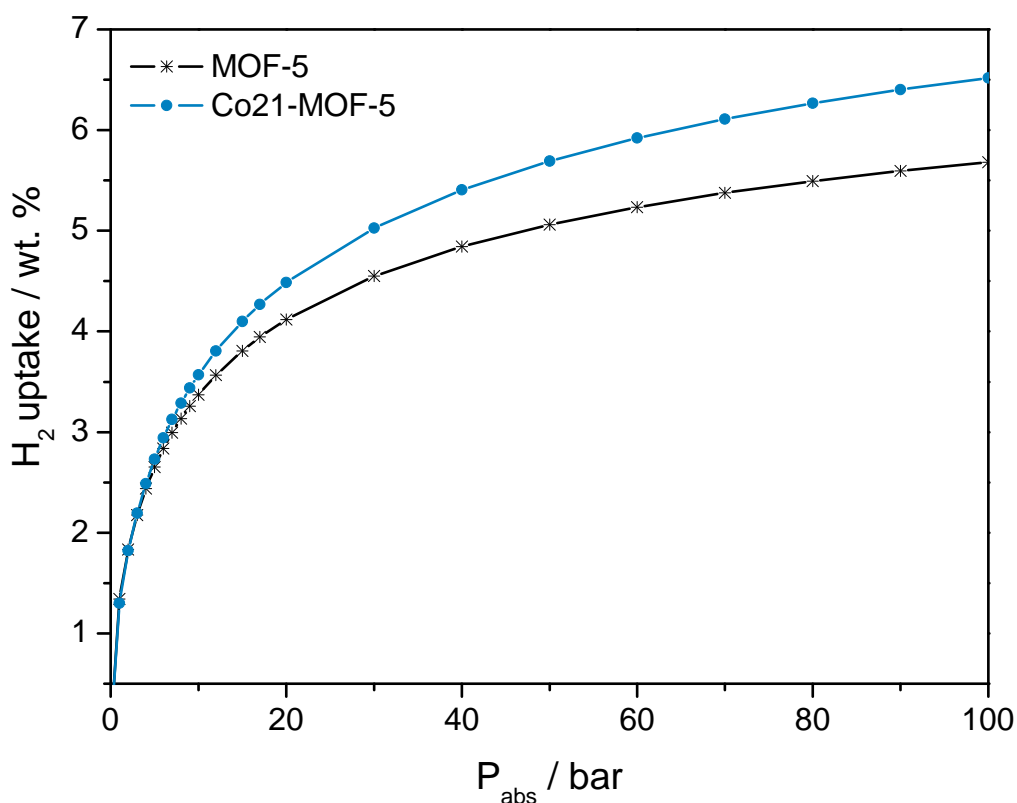

Figure S3C. Sips fit to H$_2$ adsorption isotherms at 77 K for sample Co21-MOF-5.

This suitable model for describing adsorption behavior in microporous materials, at low and high pressure, was used to fit experimental points of hydrogen adsorption isotherms at 77 K. In other to quantify this deviation from ideality, Chi-Square and R-Square parameters were calculated for the three samples (Table S1). Taking into account that best fit corresponds to $Chi^2/DoF = 0$ and $R^2 = 1$, the results indicate that Sips model fits very well the experimental data for all samples. However, higher deviation for isotherms of Co-contained samples is found. Such deviation is higher for higher Co content. Observed behavior suggests an extra contribution in the isotherms of these samples, which should be responsible for the enhancing of H_2 uptake at high pressure with respect undoped MOF-5.

Table S1. Chi-Square and R-Square parameters from Sips model fit.

Sample	Chi^2/DoF	R^2
MOF-5	0.00018	0.99986
Co8-MOF-5	0.00065	0.99953
Co21-MOF-5	0.00092	0.99942

By means of these well-fits with Sips model, the isotherms were simulated up to a pressure as high as 100 bar. Figure S4 shows the results for MOF-5 and Co21-MOF-5 sample. A remarkable increase in H_2 uptake at 100 bar for Co21-MOF-5 (6.52 wt. %) with respect to undoped MOF-5 (5.68 wt. %) material was predicted.


Figure S4. Simulated high pressure H_2 adsorption isotherms at 77 K for MOF-5 and Co21-MOF-5 samples.

Isosteric heat of adsorption

The isosteric heat of adsorption (-ΔH_{ads}) was calculated by using the Clausius–Clapeyron equation[1] from the H_2 adsorption isotherms at 77 and 87 K. The isosteric heat of adsorption in dependence of the surface coverage θ is expressed as:

$$\Delta H_{ads} = -R\left(\frac{\partial Ln(P)}{\partial \left(T^{-1}\right)}\right)_{\theta}$$

in which, P, R, and T are the pressure, gas constant and temperature, respectively. ΔH_{ads} values can be obtained from the slope of the plot Ln(P) Vs 1/T. The plot of the heat of adsorption values *versus* H_2 coverage for the different materials displays just light variations at low H_2 uptakes, which tend to equalize at higher coverages. These similar values in the isosteric heat of adsorption might be for the lack of having exposed or unsaturated metal sites in the MOF-5 structure, irrespective to the nature of metal in the inorganic clusters, introducing just little changes in H_2-framework binding. Furthermore, since all studied materials have analogous pore dimensions, it is expected to find similar van der Waals forces of neighboring atoms.
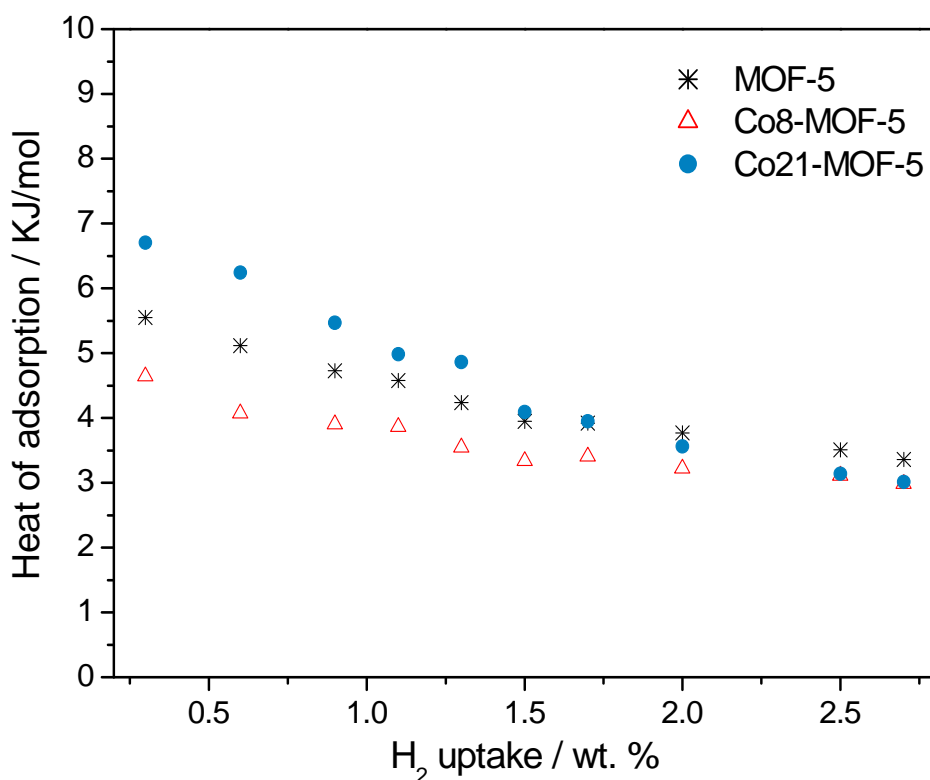
Figure S5. Isosteric heats of H_2 adsorption of MOF-5, Co8-MOF-5 and Co21-MOF-5 samples at different coverages.

(1) B. Schmitz, U. Müller, N. Trukhan, M. Schubert, G. Férey, and M. Hirscher, *ChemPhysChem*, 2008, **9**, 2181.