

Electronic Supplementary Information

General Methods and Experimental Conditions

MIL-101(Cr) was prepared by direct hydrothermal synthesis, mixing chromium(III) nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, hydrofluoric acid with 1,4-benzenedicarboxylic acid H_2BDC , according to Férey's method.¹

MIL-101(Fe) was prepared electrochemically using pure aluminium electrodes with a surface of 4.9 cm^2 . The electrodes were immersed in 100 cm^3 of N,N-dimethyl formamide a solution of 1.5 g 1,4-benzenedicarboxylic acid and 4.5 g tributylmethylammonium methyl sulphaten. A constant current of 20 mA was applied for 3h at $95 \text{ }^\circ\text{C}$, similarly to what was reported by Martinez-Joarasti *et al.*²

Cation exchange was carried out as follows: 100 mg MIL-101(Cr) was refluxed for 3 days with *ca.* 5 mg AlCl_3 or *ca.* 10 mg $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, in 100 cm^3 de-ionised water at $100 \text{ }^\circ\text{C}$. In addition, 100 mg MIL-101(Cr/Fe) was refluxed for 3 days with *ca.* 5 mg AlCl_3 in 100 cm^3 de-ionised water at $100 \text{ }^\circ\text{C}$. Samples were subsequently filtered on air, refluxed with 50 cm^3 anhydrous THF at $100 \text{ }^\circ\text{C}$ overnight in order to remove the residual guest from the pores and filtered again. Samples were activated *in vacuo* at $160 \text{ }^\circ\text{C}$ for 16 h before adsorption experiments.

Structural analysis was performed with a Bruker D8 Advance X-ray diffractometer (Co- K_α , $\lambda=0.178897 \text{ nm}$) equipped with a LynxEye detector in the Bragg-Brentano configuration.

UV-Vis diffuse reflectance spectra were measured with a Perkin-Elmer Lambda 900 spectrophotometer equipped with an integrating sphere ("Labsphere") in the 200–800 nm range. Kubelka-Munk function was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of BaSO_4 as reference.

N_2 adsorption at 77 K was measured in a Quantachrome Autosorb - 6B unit gas adsorption analyser. The specific BET surface area was calculated between 0.05-0.15 relative pressures.

Hydrogen adsorption and desorption isotherms were recorded at 298 and 77 K, in a Sievert's apparatus (HyEnergy, PCTPro-2000) up to *ca.* 45 bar hydrogen pressure. Due to their sensitivity towards moisture, the activated samples were loaded into the microdoser in a glove box, under Ar atmosphere.

Elemental analysis was carried out by means of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Approximately 50 mg sample was destructed in $4 \text{ cm}^3 \text{ HCl} + 2 \text{ cm}^3 \text{ HNO}_3$, using a microwave oven. After destruction the samples were diluted to 50 cm^3 with MQ water. For Cr analysis, the samples were diluted 1:10. The procedure was carried out *in duplo* with the average taken as result.

Transmission ^{57}Fe Mössbauer spectra were collected at room temperature with a conventional constant-acceleration spectrometer using a $^{57}\text{Co}(\text{Rh})$ source. Velocity calibration was carried out using an $\alpha\text{-Fe}$ foil. The Mössbauer spectra were fitted using the Mosswin 3.0i programme.³

Table S1 Substituent metal atom content of SACS-modified MIL-101(Cr), content is given as the atom percentage of the substituent metal ions with regards to the total number of metal ions in the framework

	MIL-101(Cr/Fe)	MIL-101(Cr/Fe/Al)	MIL-101(Cr/Al)
Al, metal ion %	-	12.5(6)	10.2(5)
Fe, metal ion %	5.8(4)	3.8(5)	-

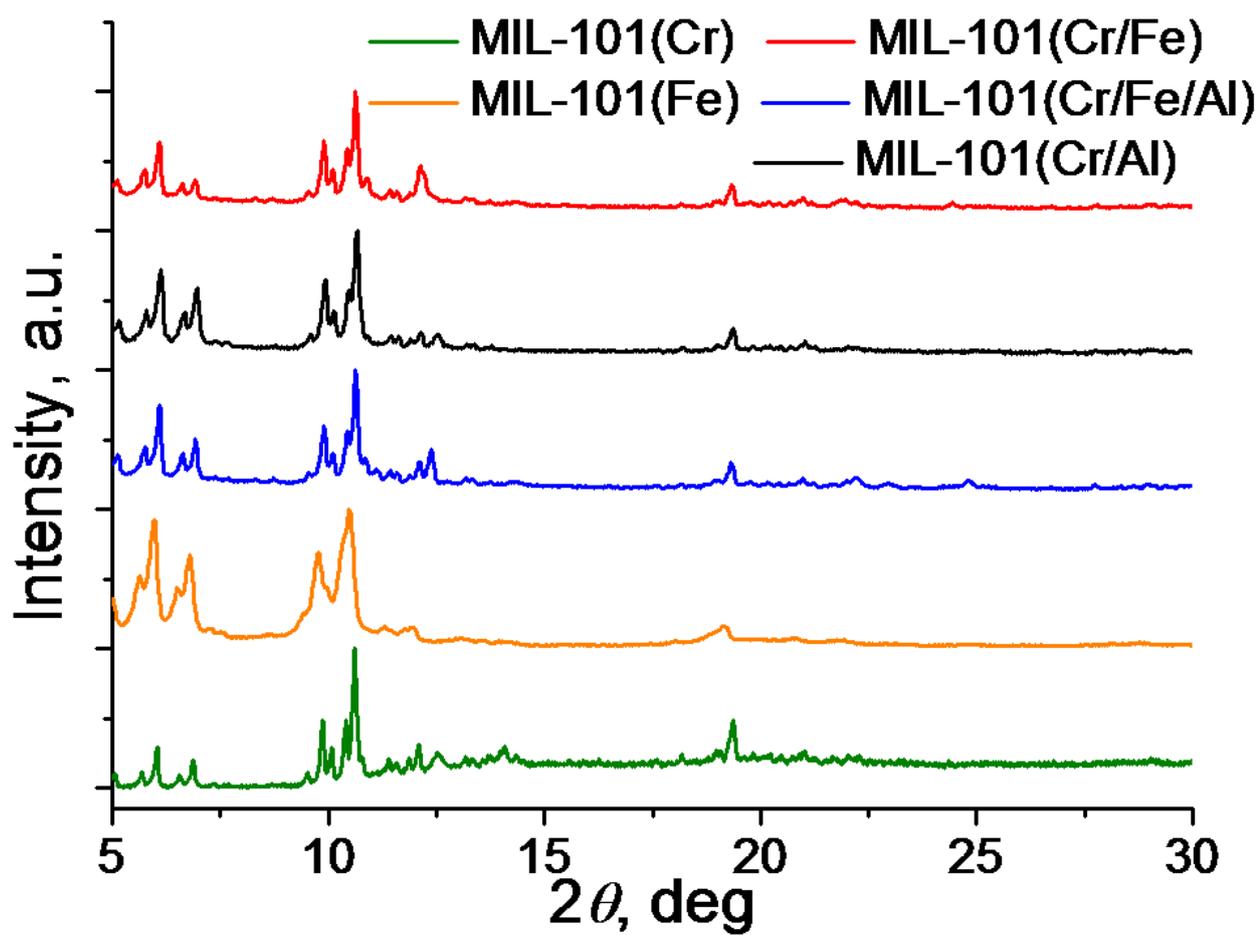


Figure S1 Powder X-ray diffraction patterns of the MIL-101 samples at 298 K

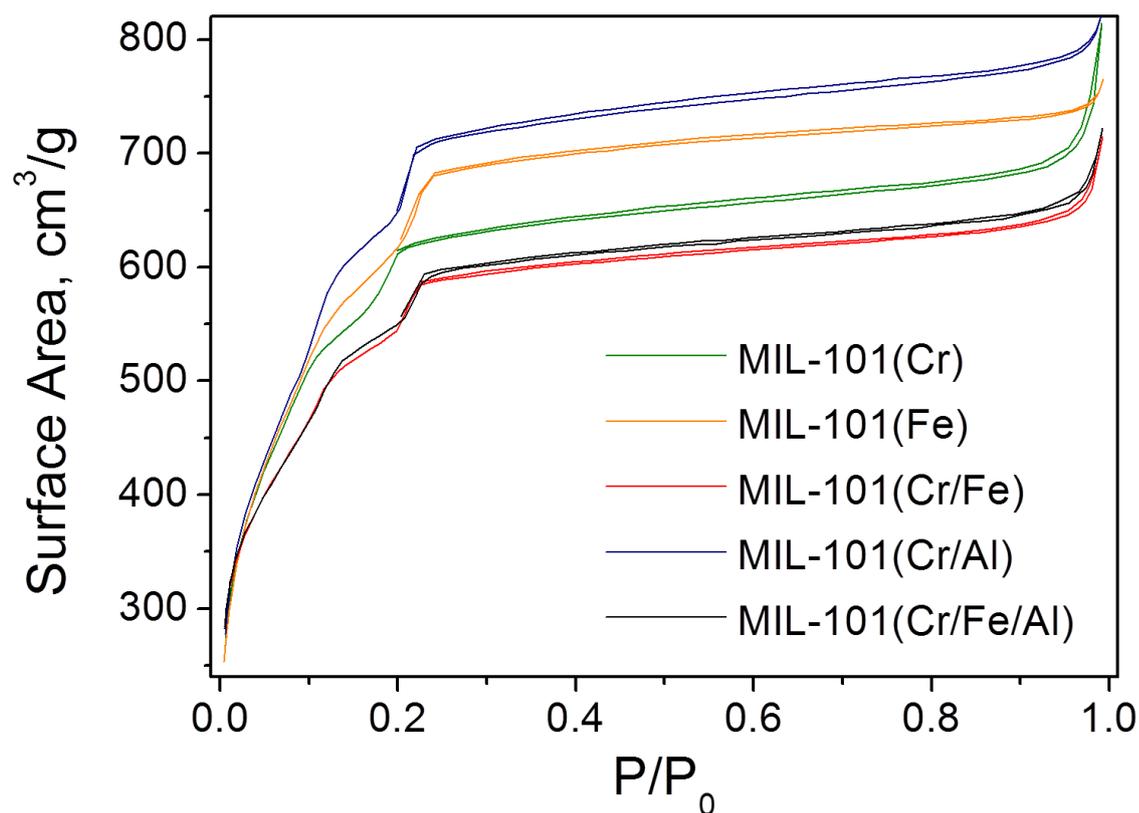


Figure S2 Nitrogen sorption isotherms of MIL-101 samples at 77 K

Table S2 Brunauer-Emett-Teller areas of the MIL-101 samples as determined by 77 K N₂-adsorption

BET, m ² g ⁻¹	MIL-101(Cr)	MIL-101(Fe)	MIL-101(Cr/Fe)	MIL-101(Cr/Fe/Al)	MIL-101(Cr/Al)
	2230	2395	1830	1838	2644

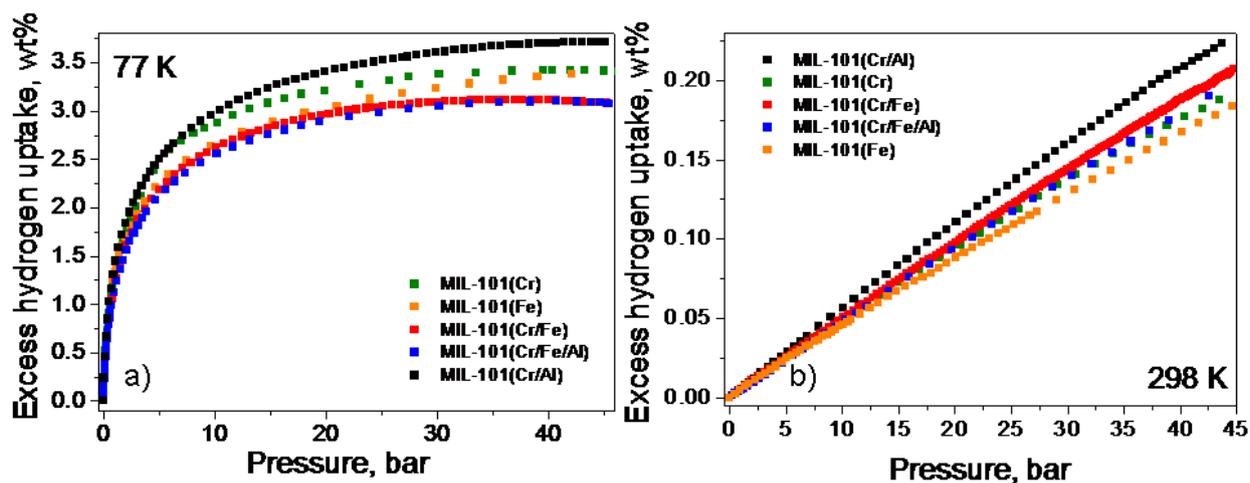


Figure S3 Hydrogen adsorption isotherms of MIL-101 samples at a) 77 K and b) 298 K

References

- 1 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.
- 2 A. Martinez Joaristi, J. Juan-Alcañiz, P. Serra-Crespo, F. Kapteijn and J. Gascon, *Cryst. Growth Des.*, 2012, **12**, 3489.
- 3 Z. Klencsár, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 1997, **129**, 527.