

Supporting information

Guest-induced breathing mediated selective alcohol recovery from water by MIL-88A(Fe)

Nagore Barroso^a, Subhajit Dutta^a, Jacopo Andreo^a, Garikoitz Beobide^{a,b}, Oscar Castillo^{a,b,*}, Antonio Luque^{a,b}, Sonia Pérez-Yáñez^{a,b} and Stefan Wuttke^{a,c,*}

^a*BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48950 Leioa, Spain*

^b*Organic and Inorganic Chemistry Department, University of the Basque Country, UPV/EHU, Barrio Sarriena s/n, 48950 Leioa, Spain*

^c*IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain*

**Correspondence: oscar.castillo@ehu.eus , stefan.wuttke@bcmaterials.net*

EXPERIMENTAL PROCEDURE

Chemicals: For the synthesis of MIL-88A(Fe) the following chemicals were used: iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99+% extra pure) and fumaric acid (99+%) were purchased from Across Organics and N,N-dimethylformamide (DMF, 99.9% GLR) from Chemlabs. PVDF (Solef®1010) was purchased from Solvay. All alcohols were purchased from Sigma.

Characterization: The crystallinity and purity of the samples were assessed by powder X-ray diffraction (PXRD). PXRD patterns were collected on a Philips X'PERT powder diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) over the $5 < 2\theta < 40^\circ$ range with a step size of 0.02° and an acquisition time of 2.5 s per step at 25°C . Fourier transform infrared spectroscopy (ATR FT-IR) measurements were performed on a Bruker Alpha Series FT-IR spectrometer equipped with an attenuated total reflectance (ATR) module by collecting 16 scans of MIL-88A(Fe) in the ATR module to ensure the chemical stability of the sample after the cycling. Scanning electron microscopy (SEM) was used to determine particles size and morphology. For that, samples were coated with a thin gold layer and measured on a Hitachi S-4800 scanning electron microscope (150 s, 20 mA, 10 kV, zoom at $\times 10.000$). Magnetic sustentation experiments were performed using a dipole electromagnet (Newport Pagnell England Electromagnet Type C sourced by a Hewlett Packard 6655A System DC Power Supply) in order to determine the critical magnetic field of MIL-88A(Fe). Briefly, 15 mg of MOF were placed in a 1.5 mL water or alcohol containing aqueous solutions and were kept 24 h under rotating agitation. Afterwards, MIL-88A(Fe) crystals were placed in a 13 mm diameter test tube filled with distilled water. The critical magnetic field of the pristine MIL-88A(Fe) and after the capture of the short chain alcohols from aqueous solution was determined. Each measurement was repeated 5 times in order to provide the corresponding associated error. In order to test the recyclability, MIL-88A(Fe) samples were treated under high vacuum, after each cycle, to eliminate all the molecules trapped in the pores. A series of additional adsorption experiments were designed in which two consecutive single alcohol adsorption experiments were performed (each one of 24 h) alternating between branched (*t*-BuOH and *s*-BuOH) and small linear alcohols (MeOH and EtOH). The determination of the critical magnetic field in the consecutive adsorption experiments was performed as previously described. Kinetic adsorption curve was prepared similarly, but in this case, the same methanol-water mixture employed for the adsorption procedure was used as the liquid media. Gravimetric vapour adsorption measurements were performed placing 20 mg of degasified MIL-88(Fe) for a specific time in a close vessel containing an alcohol saturated atmosphere and measuring its weight at different times. Pore-size distribution (PSD) data of MIL-88A(Fe) (open and close configurations) were computed using Poreblaze 4.0 an open-source Fortran 90 code to calculate structural properties of porous materials.¹ The structural models for the MOF structures were taken from their crystallographic information files,² from which solvent molecules were removed

prior to run the calculations. Force-field based Grand Canonical Monte Carlo (GCMC) simulations of methanol and *tert*-butyl alcohol adsorption were carried out using the SORPTION module included in the Accelrys “Materials Studio” package.³ The theoretical background of GCMC simulations is described in detail elsewhere.⁴ Dispersive and electrostatic interactions were considered in all simulations. Dispersive interactions were modelled using a Lennard-Jones 12–6 potential. Lorentz-Berthelot mixing rules were used to calculate the parameters representing the interaction between different atom types. A cut-off radius of 12.5 Å was set for dispersive interactions. Point charges were assigned to the atomic sites in order to model the electrostatic interactions, while Ewald summation was applied to consider the periodicity of the simulation box. All simulations were performed using 2x2x2 supercells of MIL-88A(Fe). The LJ parameters for all the atoms of the adsorbents were taken from the universal force field (UFF).⁵ The partial charges to represent the electrostatic potential inside the pores were derived from DFT calculations using the ESP method as described by Singh and Kollman,⁶ which is implemented in the DMOL3 code.⁷ For this calculation, the DNP basis set and the PBE exchange-correlation functional were selected. The Lennard-Jones parameters and the point charges that model the adsorbate molecules were taken from the transferable potentials for phase equilibria-united atom (TraPPE-UA) force field developed for primary, secondary, and tertiary alcohols.⁸ Fixed loading sorption simulations (single-molecule loading per calculation cell, 298 K) and fixed loading calculations (100 kPa, 298 K) involved 10 million equilibration steps and 10 million production steps.

¹H-NMR spectra were acquired in a Bruker AVANCE 500 (one-bay; 500 MHz) at 293 K. For the competitive alcohol adsorption study, 100 mg of MIL-88A(Fe), 1.5 mL of deuterated water and 3.7×10^{-4} mol of each alcohol were placed in a vial (0.23 M of each alcohol). The samples were left under continuous rotation for 24 h at room temperature (25 °C). The samples were filtered to separate the solid from the solution. To an aliquot of 650 µL of the supernatant 30 µL of sodium acetate deuterated water solution (0.45 g/L) were added. The same procedure was applied for each adsorbate but without adding the porous material (named as blank) in order to set the initial adsorbate amount in the adsorption experiment. The characteristic signals of the adsorbate and the sodium acetate obtained from ¹H-NMR measurement were employed to quantify the amount remaining in solution after 24 h of adsorption taking into account the difference with the blank. The same procedure was followed to quantify the alcohol adsorption in membranes. In this case, 12 mg of membrane were placed in a 0.1 wt% aqueous solution of methanol or ethanol and the same procedure as for the competitive adsorption studies on powder adsorbent was employed. Thermogravimetric analysis (TGA) was performed in a METTLER TOLEDO TGA/SDTA851 thermal analyser, under dynamic synthetic air atmosphere with a flow rate of 50 mL/min. The sample was heated at 5 °C/min in the temperature range 30–800 °C.

Contact angle was determined using an Ossila L2004A1-UK optical system to study the hydrophobicity of the 0, 10, 20 and 30 wt% PVDF@MIL-88A(Fe) membranes.

Figures

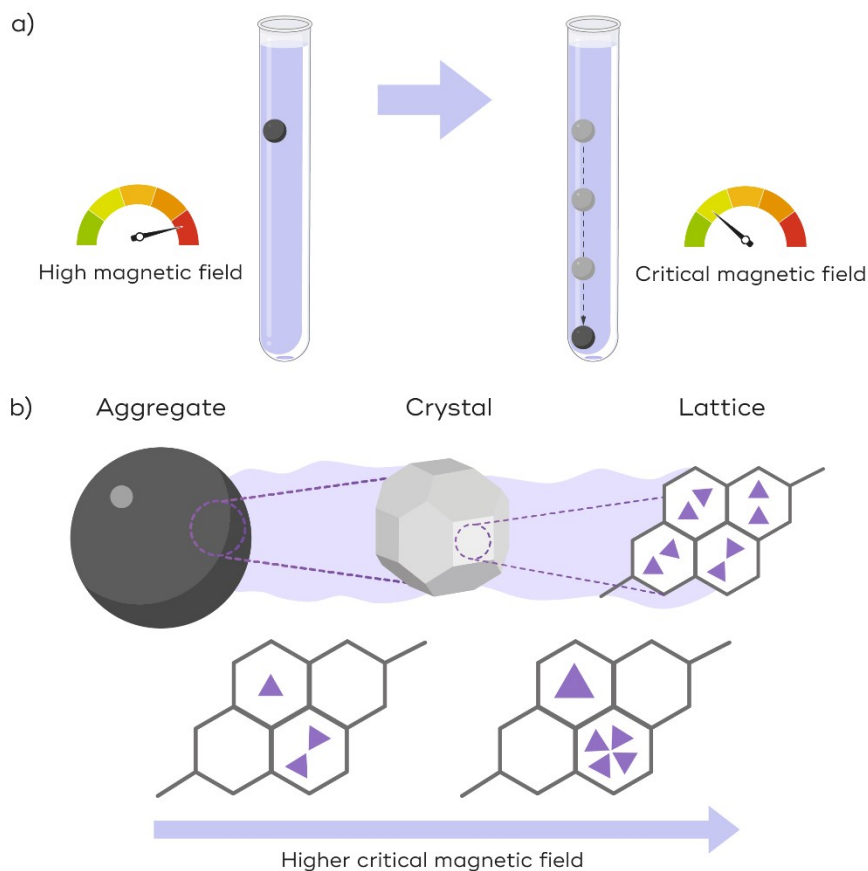


Figure S1. Scheme of the magnetic sustentation process: (a) From high magnetic field (suspended aggregate attached to the bottom of the electromagnet pole, where the magnetic force is maximum) to the critical magnetic field (aggregate dropping); (b) the MOF aggregate composition and the variation of the critical magnetic field with the guest-loaded MOF.

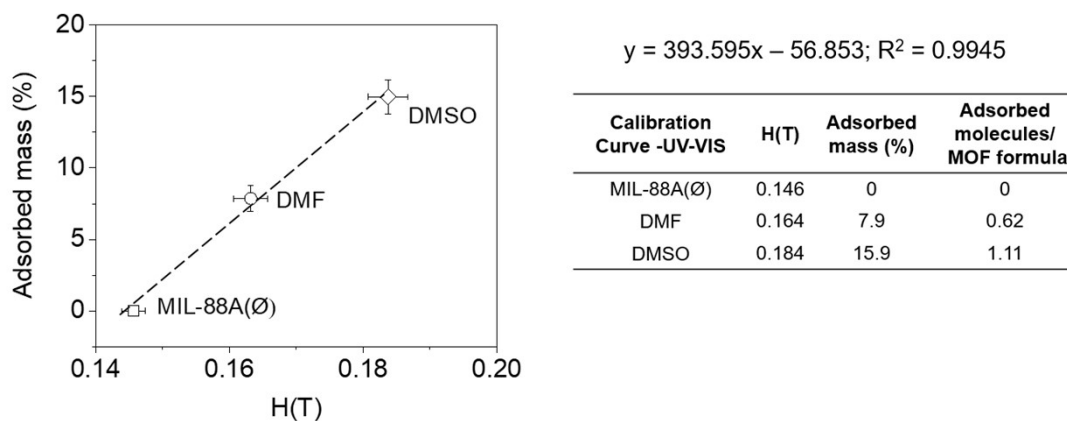
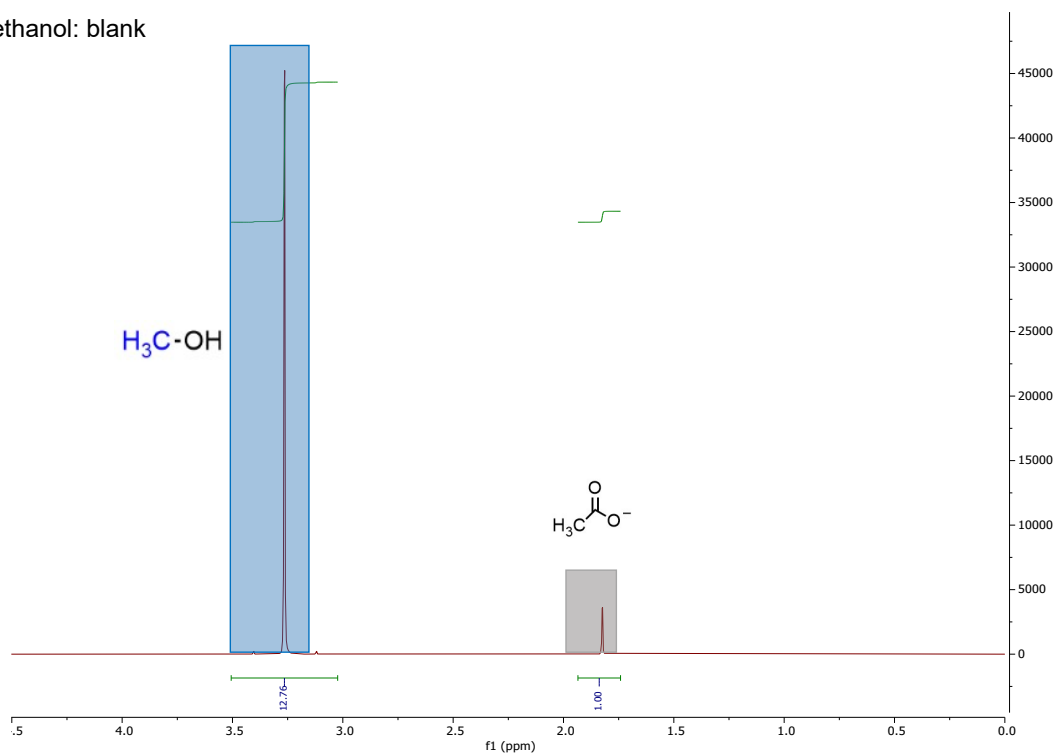


Figure S2. Calibration curve for MIL-88A(Fe) obtained from magnetic sustentation experiments and reported in our previous work⁹.

Methanol: blank



Methanol

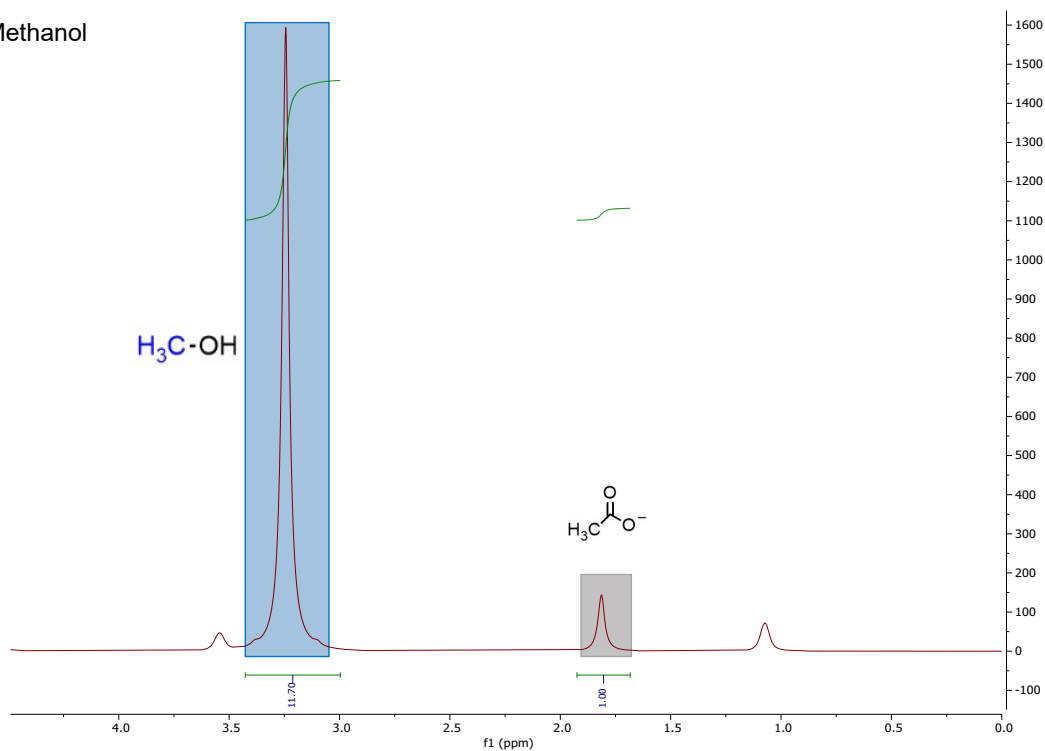
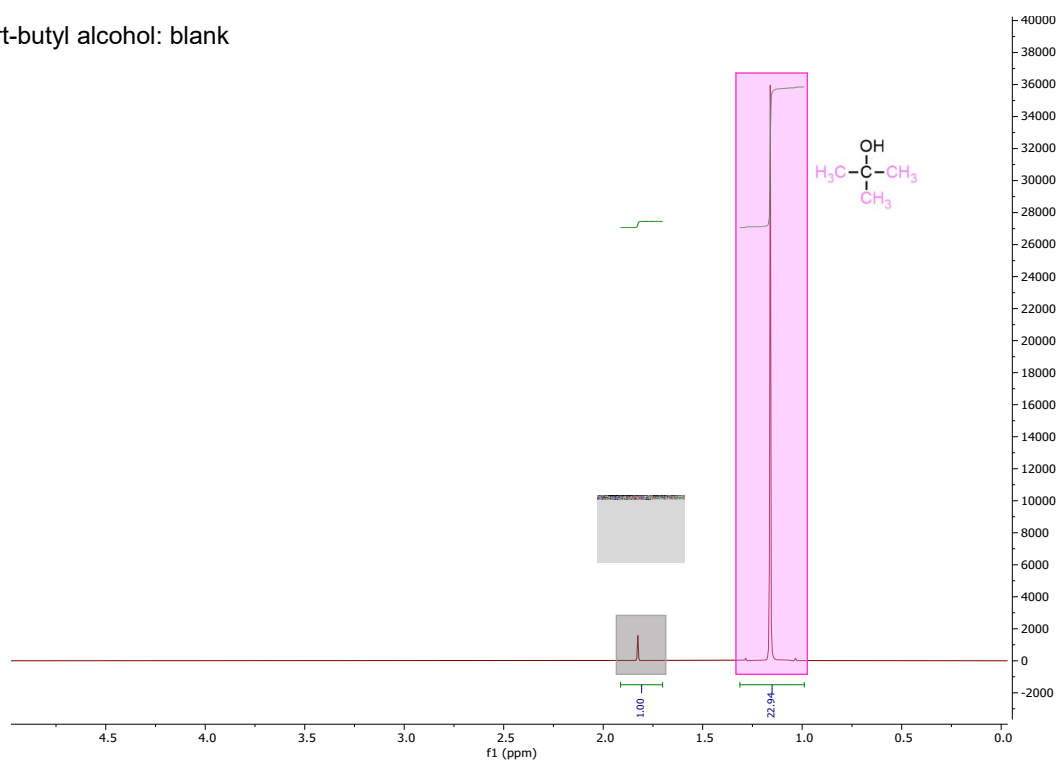


Figure S3. ¹H-NMR spectra of methanol solution (blank) and of the filtered MIL-88A(Fe) sample after 24 h of continuous stirring in methanol solution.

tert-butyl alcohol: blank



tert-butyl alcohol

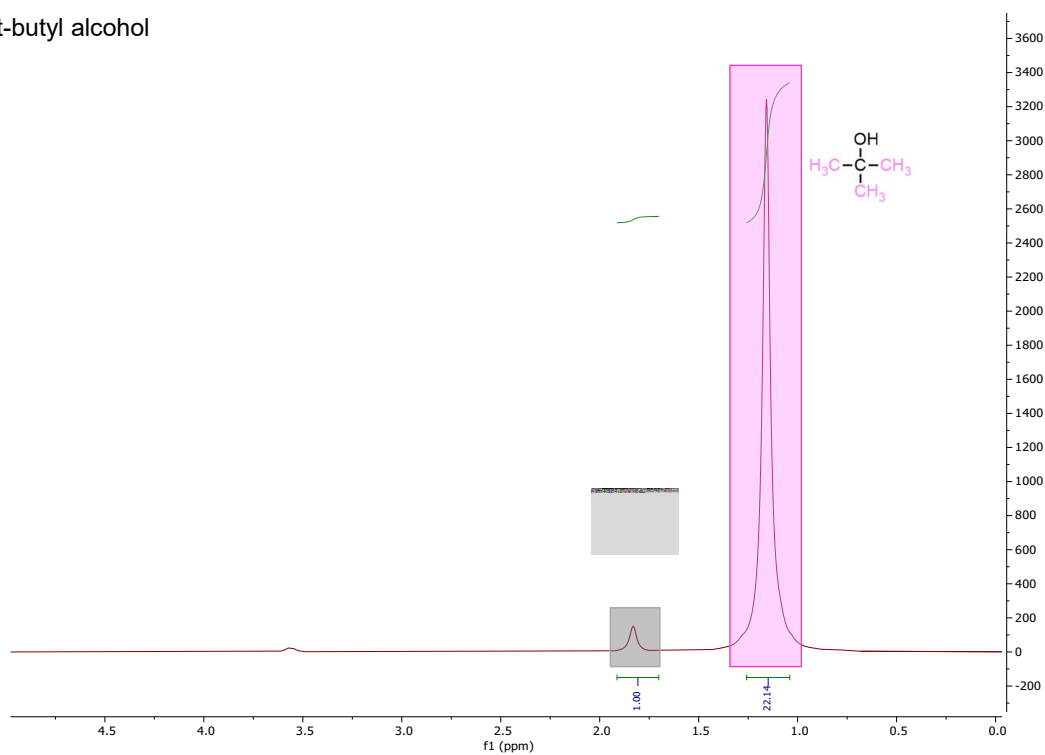
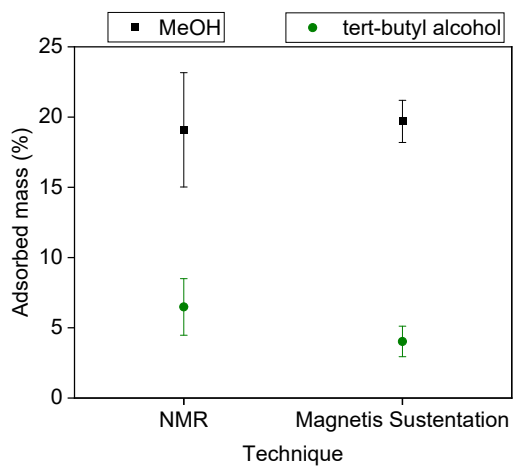


Figure S4. ¹H-NMR spectra of tert-butyl alcohol solution (blank) and of the filtered MIL-88A(Fe) sample after 24 h of continuous stirring in methanol solution.



	Magnetic Sustentation	¹ H-NMR
Methanol	19.7 ± 1.5 %	19.1 ± 4.1 %
tert-butyl alcohol	4.1 ± 1.1 %	6.5 ± 2.0 %

Figure S5. Comparison between the adsorption values and associated errors obtained from the Magnetic Sustentation technique and ¹H-NMR.

Table S1. Detailed data for the single-alcohol adsorption experiments with 50 and 200 μL of the corresponding alcohol in solution.

MOF formula: C ₁₂ H ₁₁ Fe ₃ O ₁₆	50 μL of alcohol			200 μL of alcohol			
	Adsorbate molecules	H(T)	Adsorbed mass (%)	Adsorbed molecules/MOF formula	H(T)	Adsorbed mass (%)	Adsorbed molecules/MOF formula
MeOH		0.195	19.7	3.56	0.193	18.9	3.41
EtOH		0.190	17.5	2.20	0.189	17.2	2.16
n-PrOH		0.183	14.8	1.43	0.182	14.6	1.41
n-BuOH		0.174	11.5	0.90	0.173	11.1	0.87
i-PrOH		0.169	9.4	0.91	0.168	9.1	0.88
s-BuOH		0.168	9.1	0.71	0.168	9.2	0.72
i-BuOH		0.158	5.1	0.40	0.158	5.0	0.39
t-BuOH		0.155	4.0	0.31	0.156	4.3	0.34

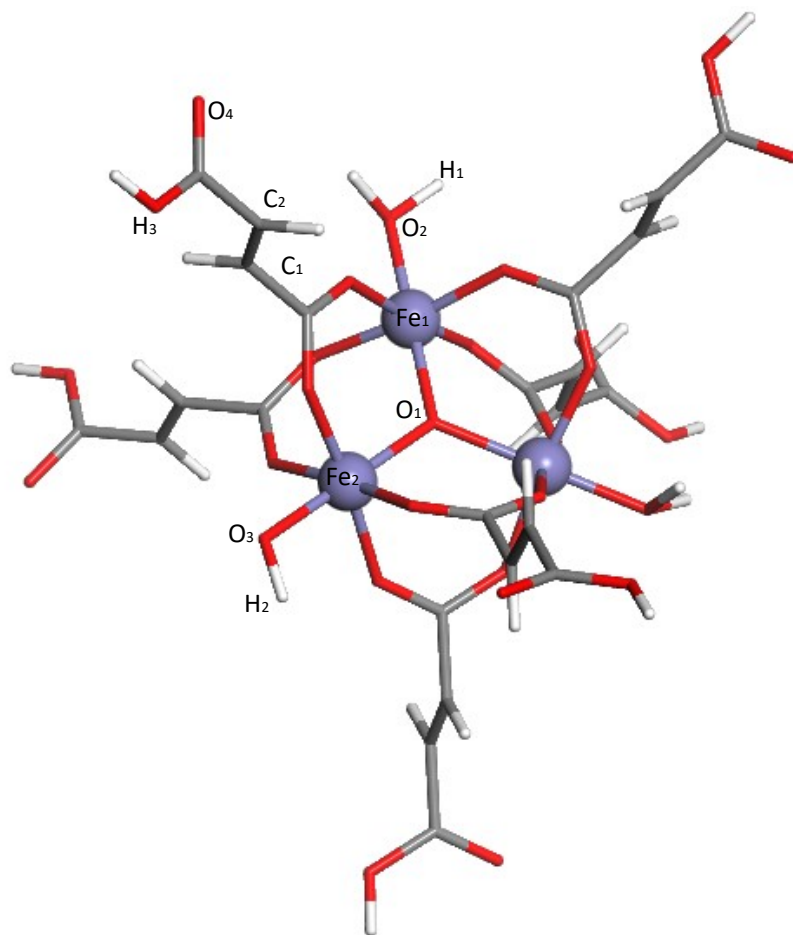


Figure S6. MOF fragment used for the DFT calculations.

Table S2. Resulting ESP-fitted charges (q/e) upon the atoms of the structure models of the adsorbents.

Atom label	Fitted charges (q/e)
Fe(1)	1,3019
Fe(2)	1,3579
O(1)	-0,9451
O(2)	-0,2746
H(1)	0,06768
O(3)	-0,3521
H(2)	0,1039
O(4)	-0,4118
C(1)	0,5289
C(2)	-0,0906
H(3)	-0,0298

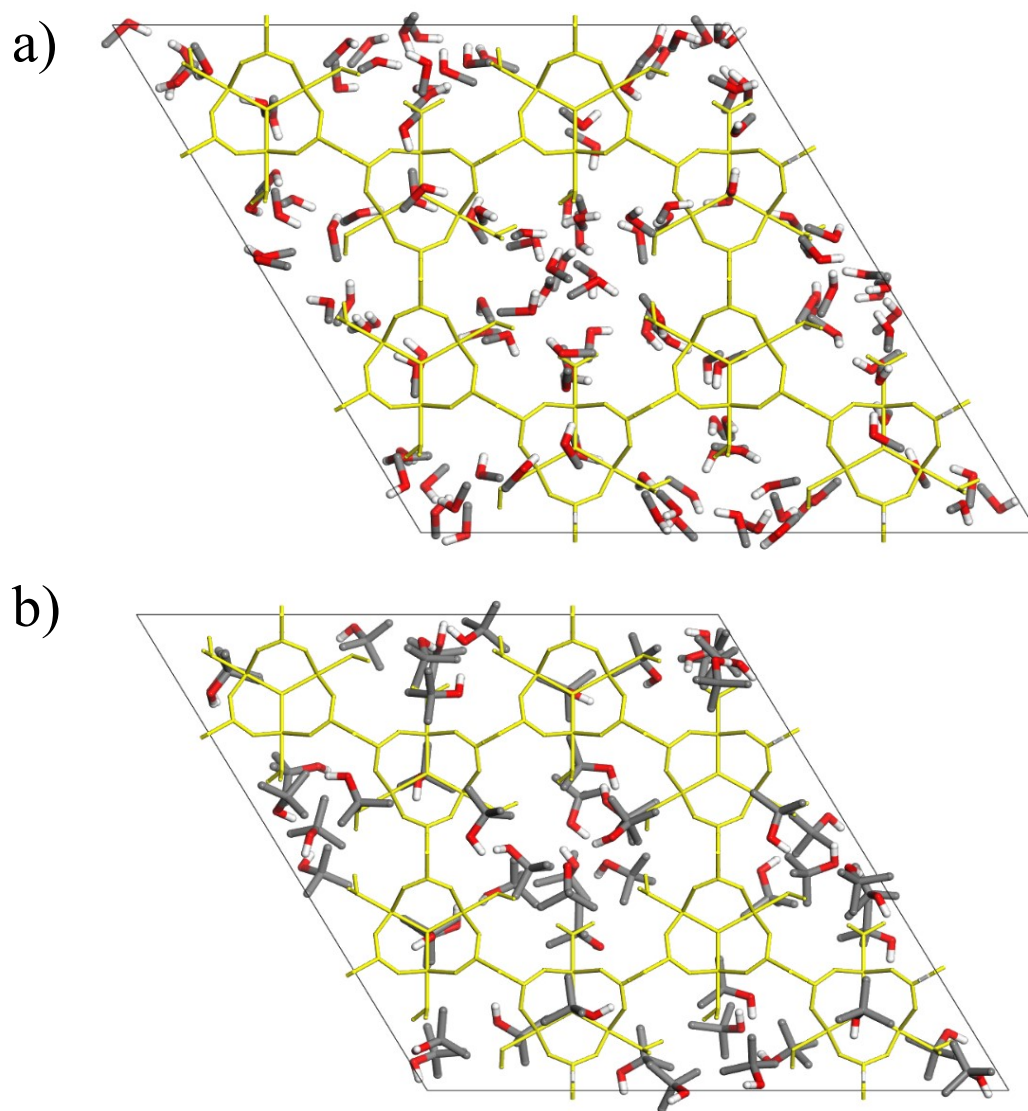
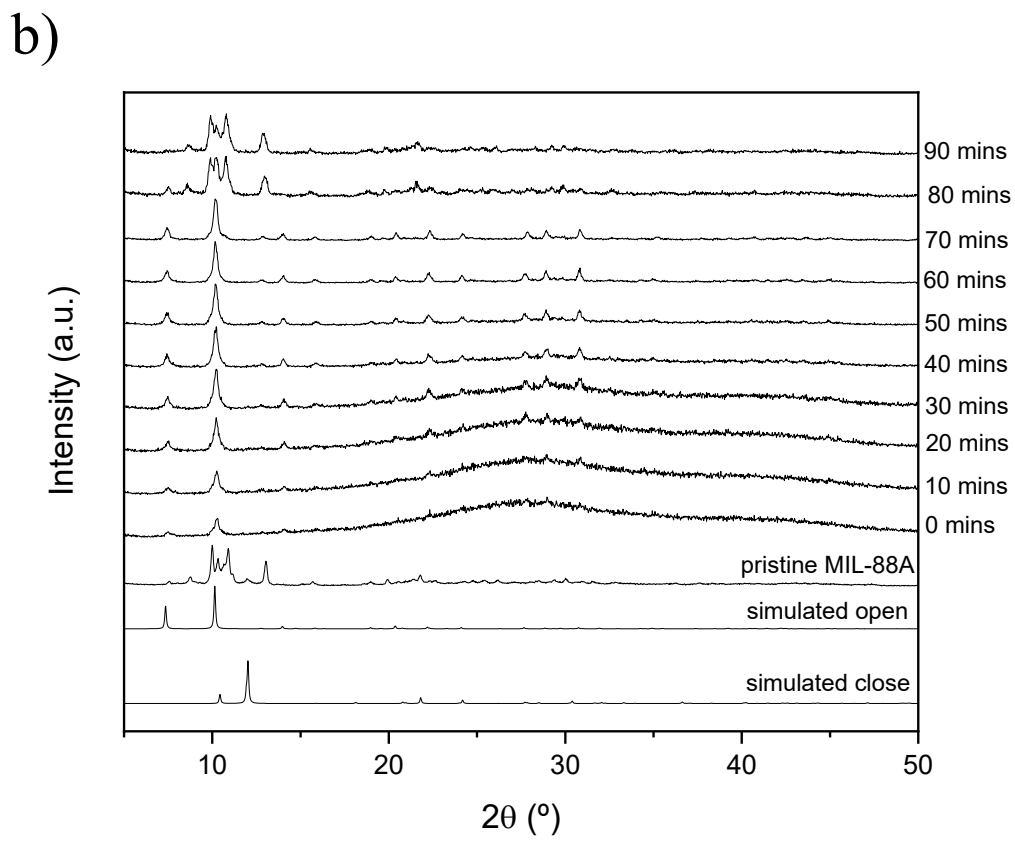
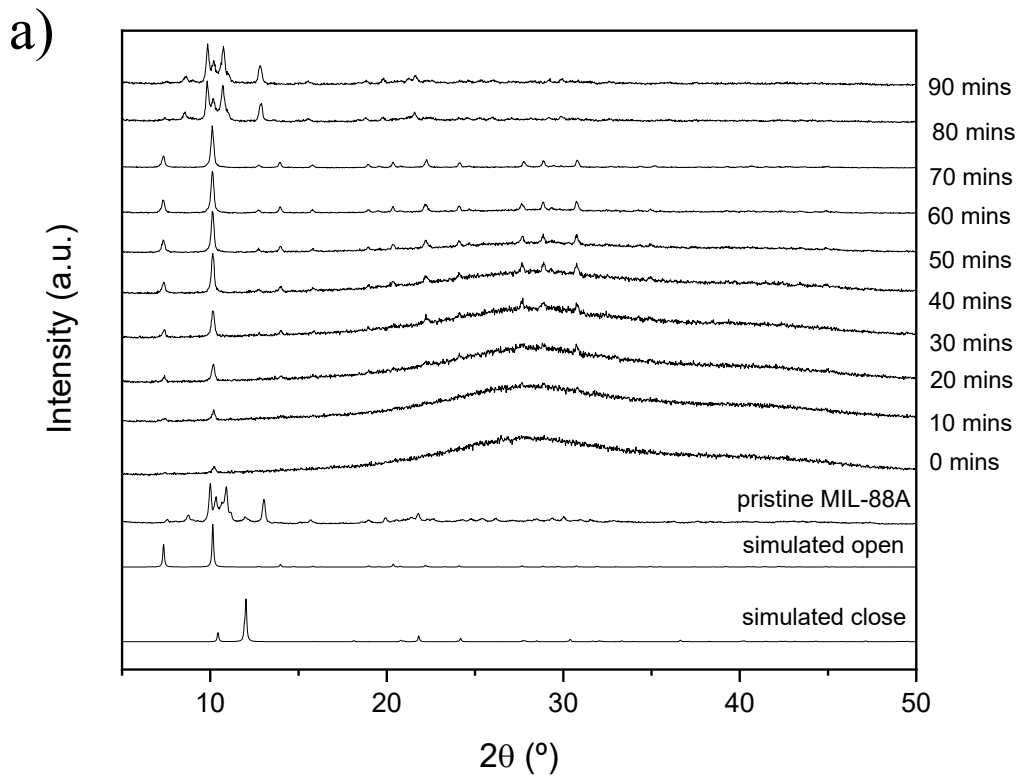
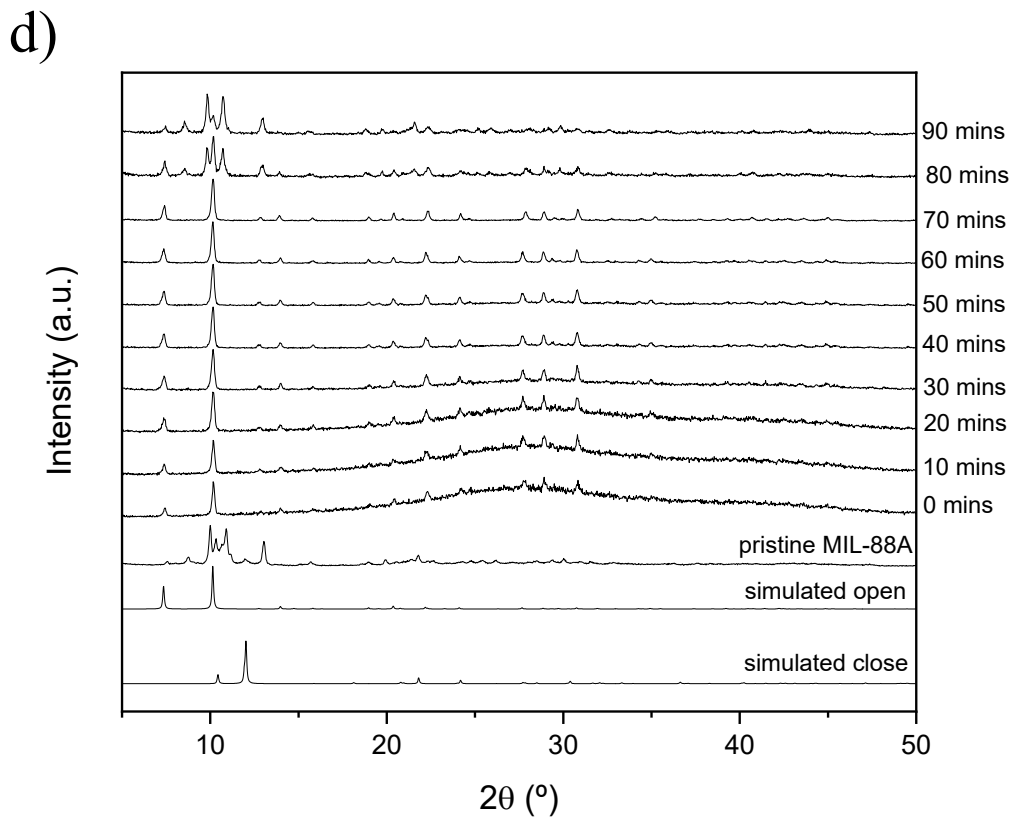
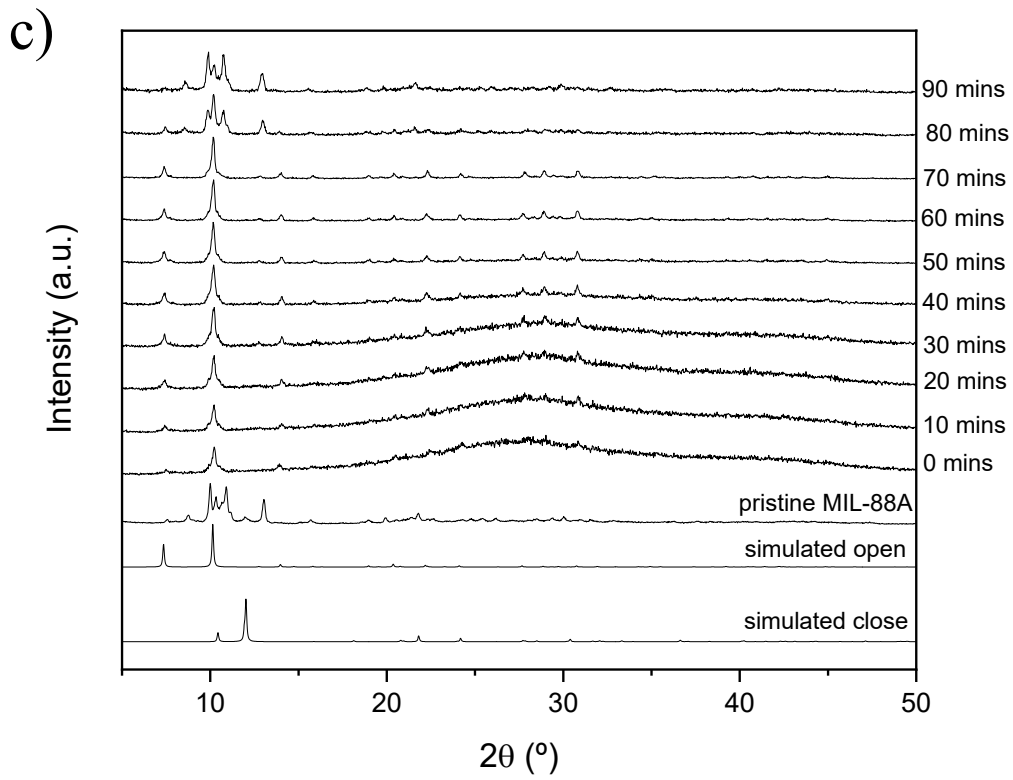
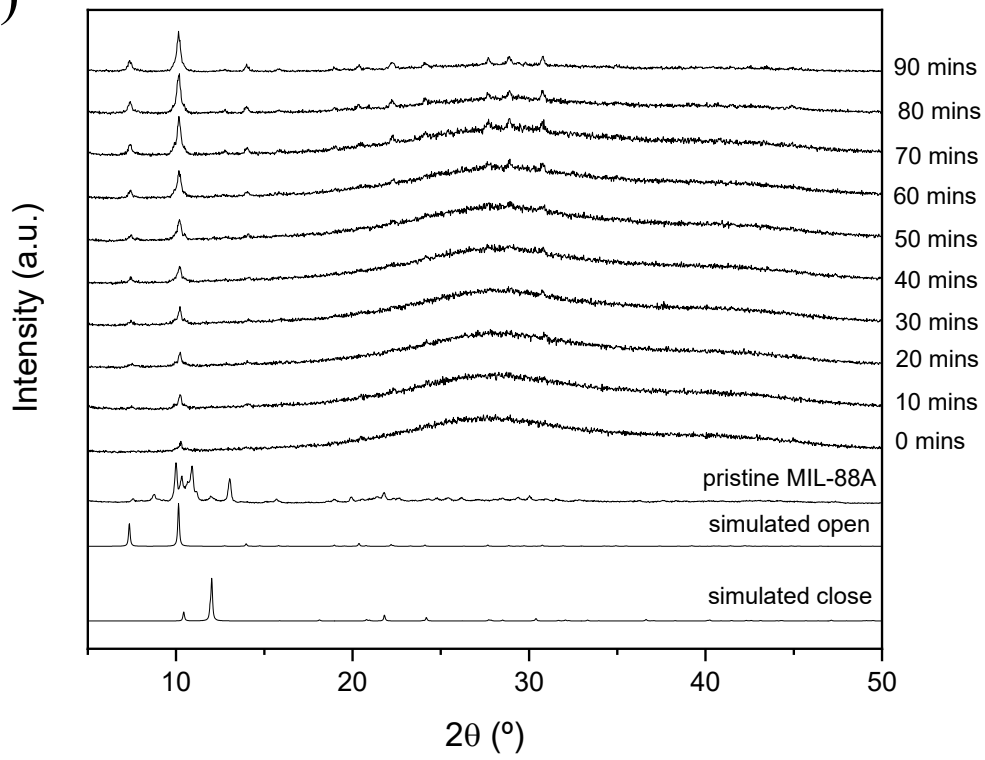


Figure S7. Lowest energy frames for fixed pressure calculation for (a) methanol and (b) *tert*-butyl alcohol (100 kPa at 298 K).

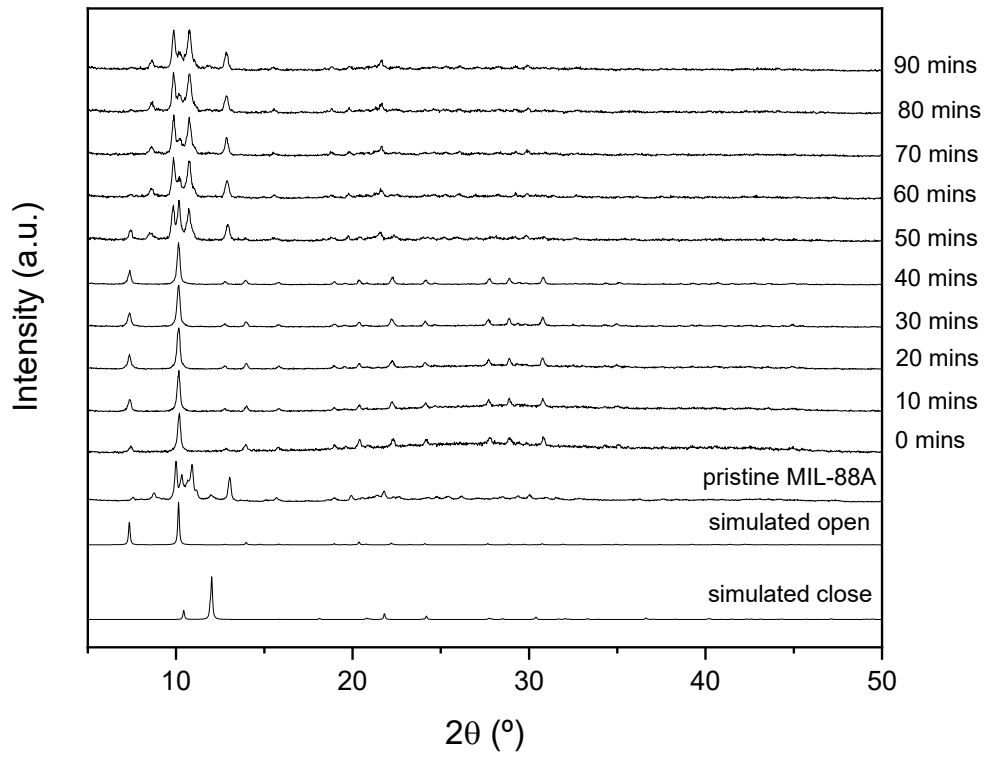




e)



f)



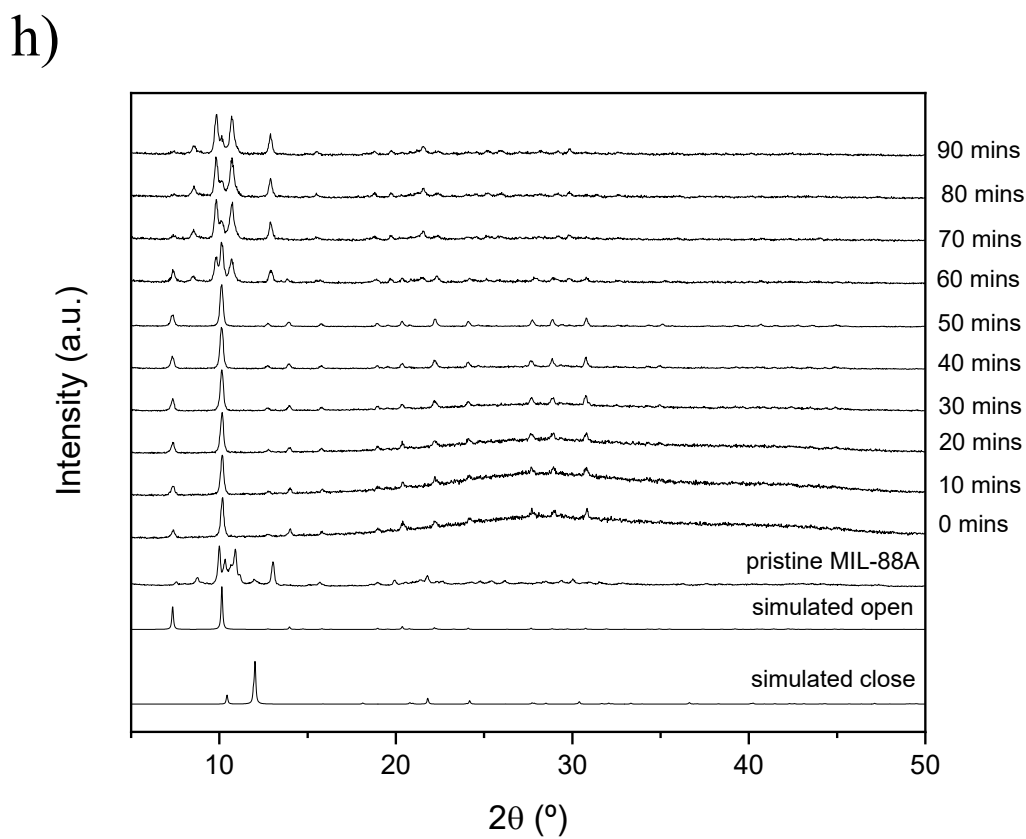
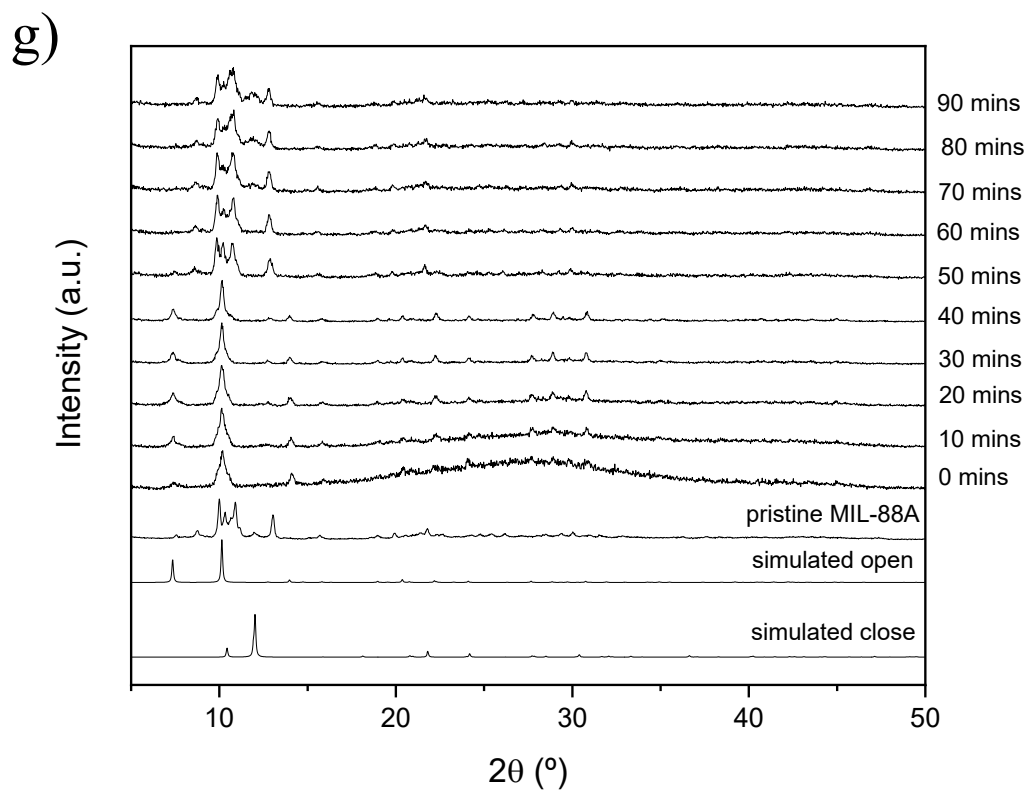


Figure S8. PXRD of wet MIL-88A(Fe) after 24 h of immersion in aqueous solutions of different alcohols: (a) methanol, (b) ethanol, (c) n-propanol, (d) isopropanol, (e) n-butanol, (f) sec-butanol, (g) isobutanol and (h) *tert*-butanol.

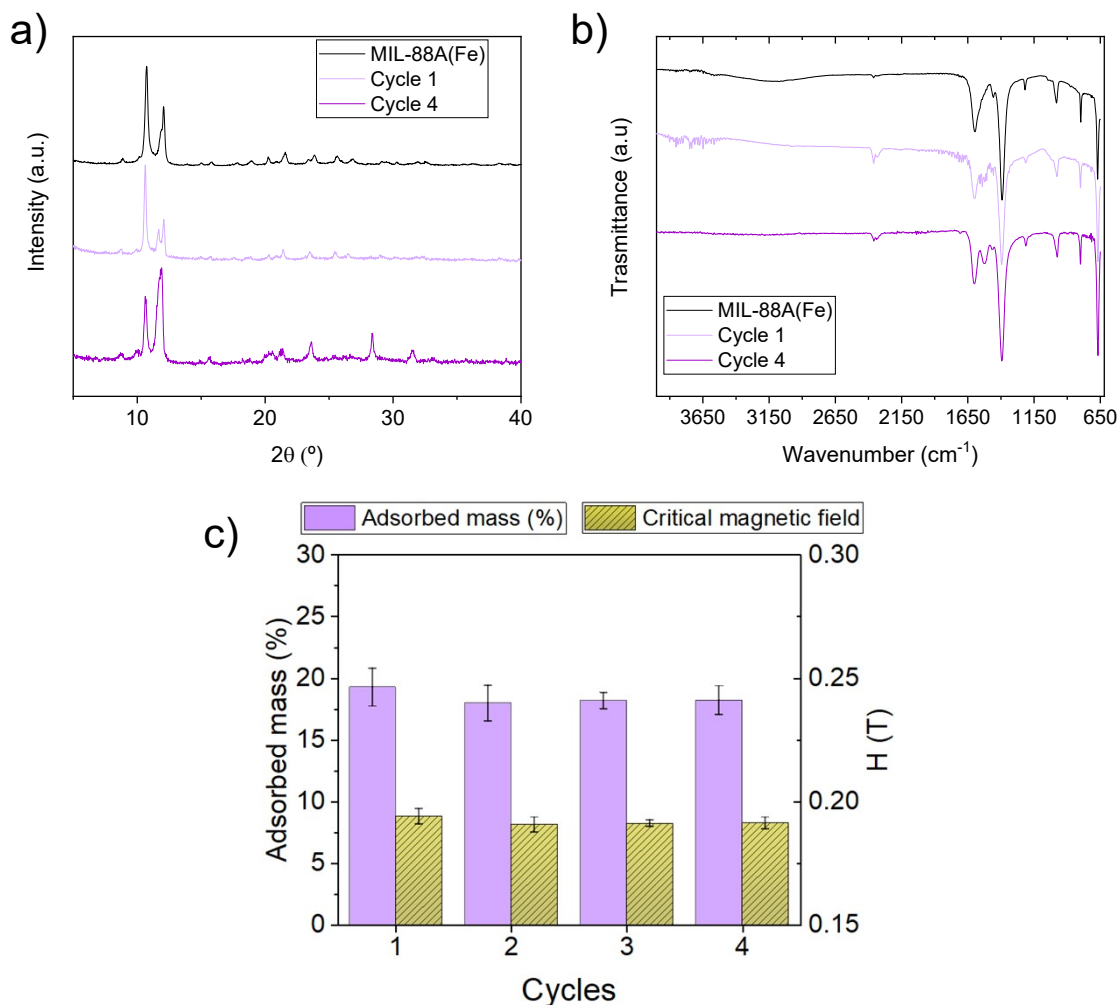


Figure S9. a) PXRD and b) FT-IR measurements for the pristine MIL-88A(Fe) and after the first and the fourth cycle. Intensity changes are attributed to different hydration status of MIL-88A(Fe). c) Recyclability of the material determined with the Magnetic Sustentation technique upon MeOH adsorption cycling.

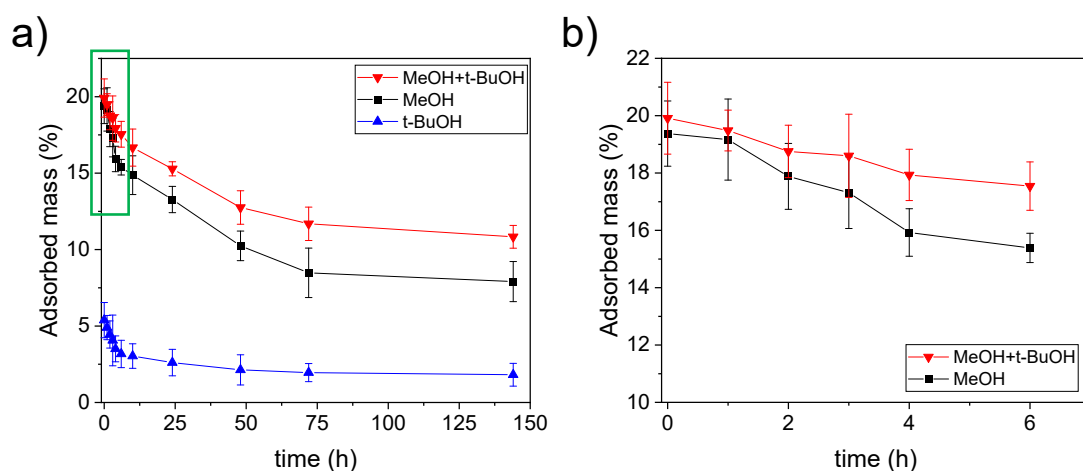


Figure S10. Desorption kinetic for t-BuOH (blue), MeOH (black) and consecutive MeOH+t-BuOH (red): a) complete desorption curve and b) zoom of the desorption curve in the range 0-6 h.

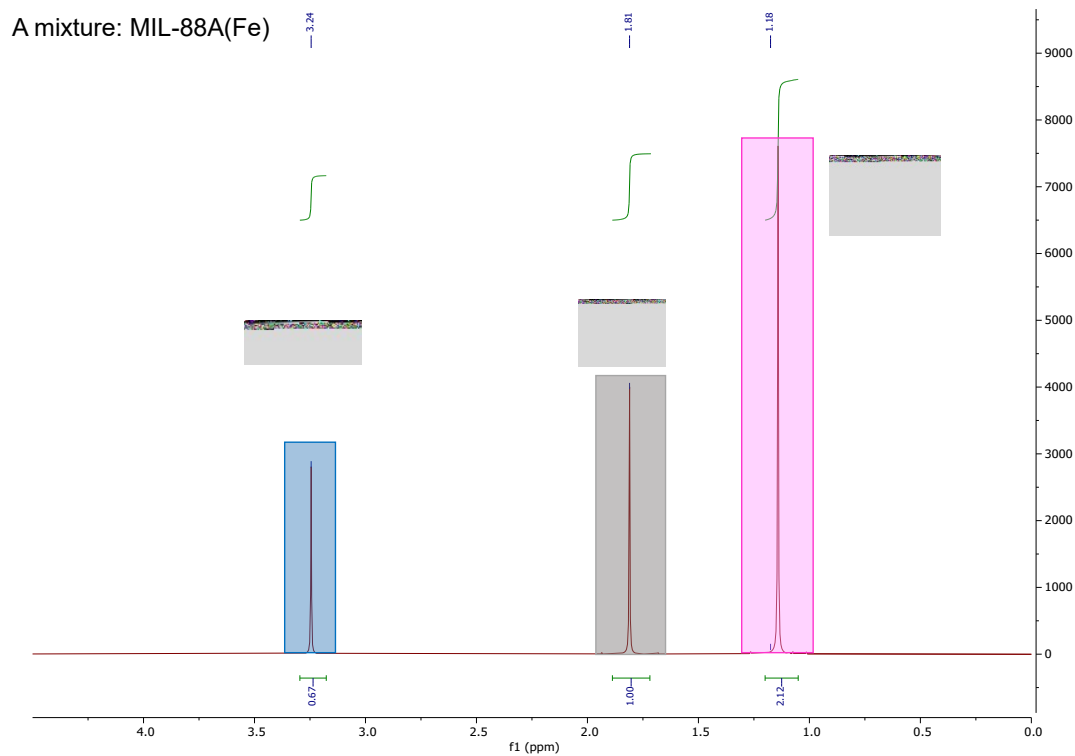
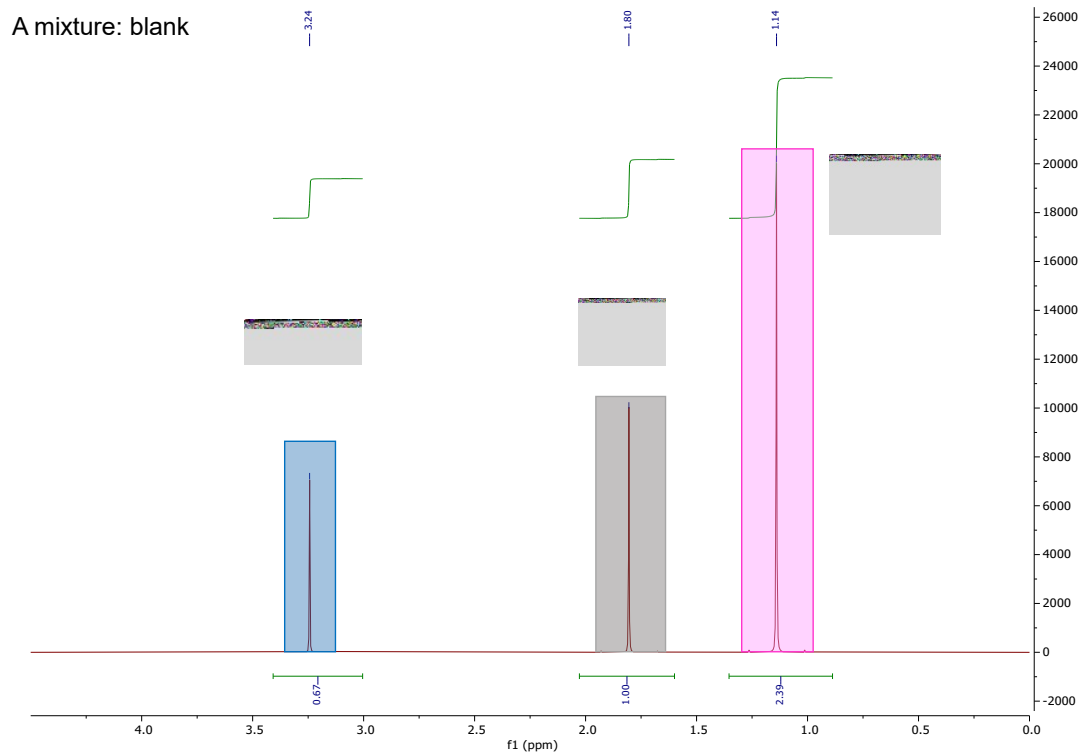


Figure S11. ^1H -NMR spectra of methanol/*tert*-butanol solution (mixture A) and of the filtered MIL-88A(Fe) sample after 24 h of continuous stirring in mixture A.

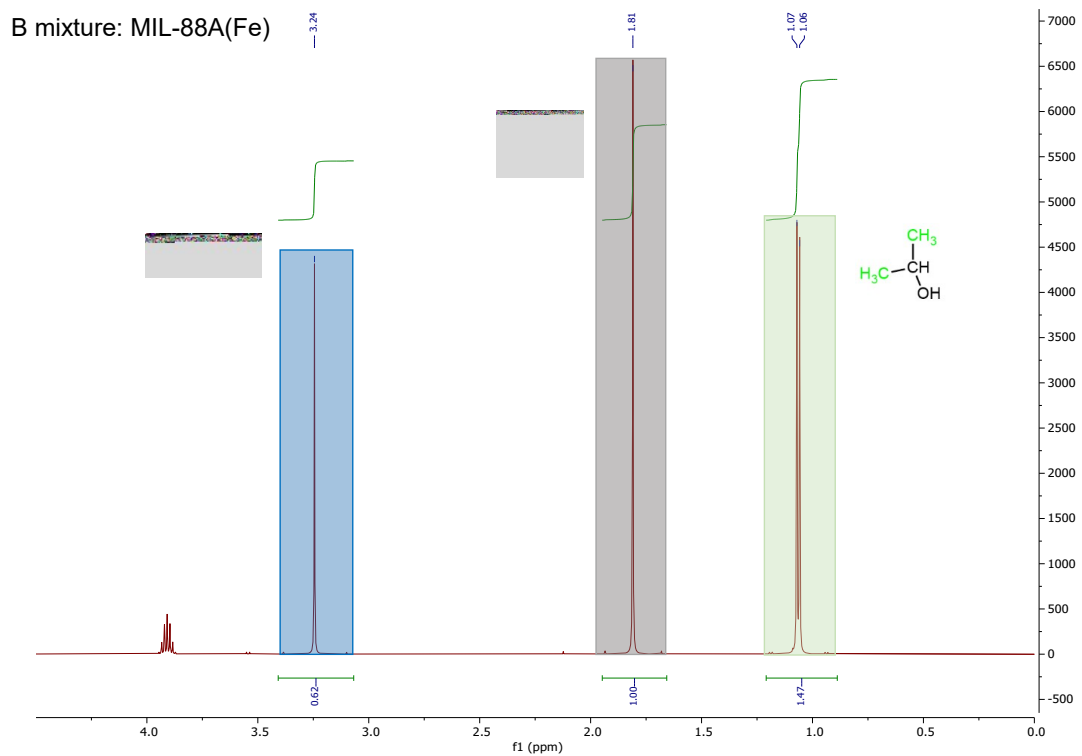
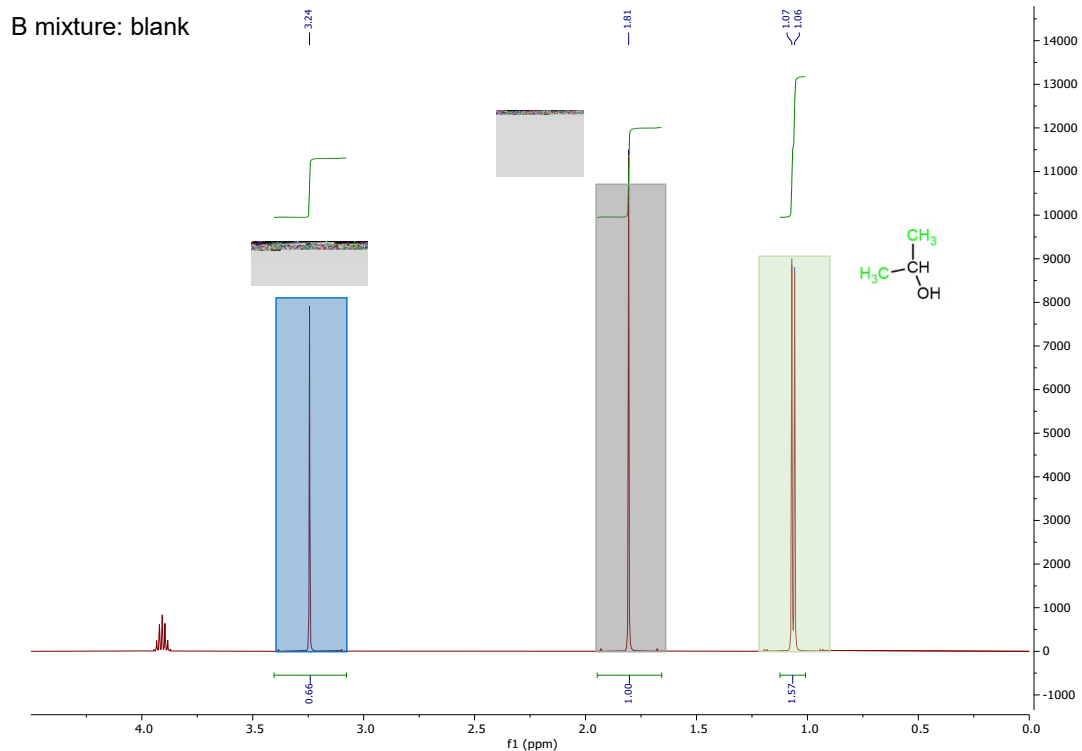
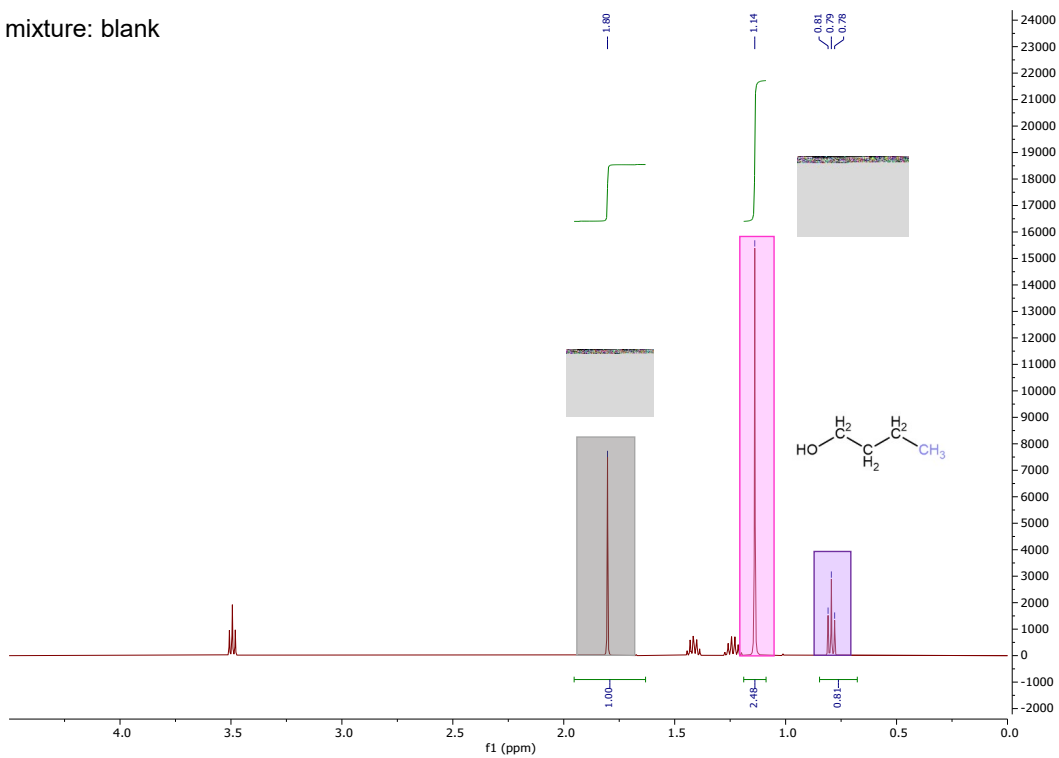


Figure S12. ^1H -NMR spectra of methanol/isopropanol solution (mixture B) and of the filtered MIL-88A(Fe) sample after 24 h of continuous stirring in mixture B.

C mixture: blank



C mixture: MIL-88A(Fe)

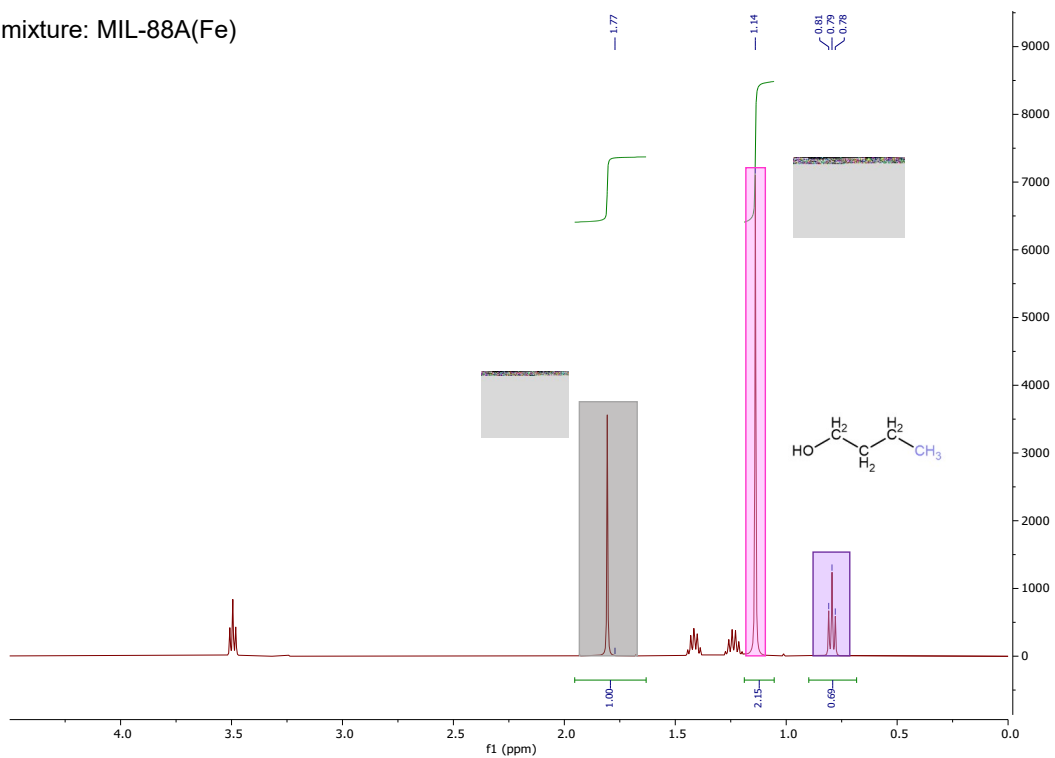
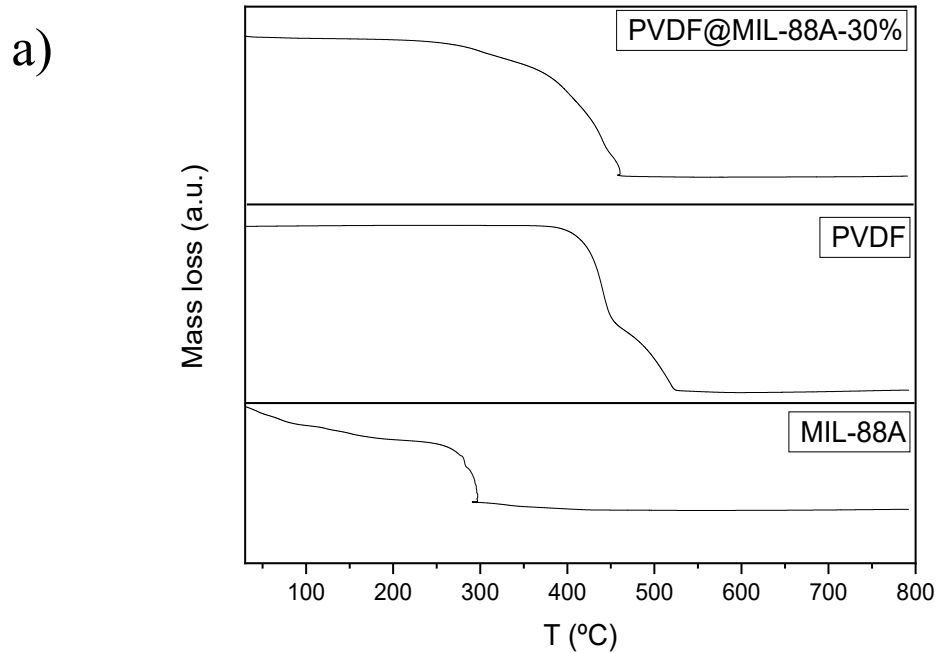


Figure S13. ¹H-NMR spectra of n-butanol/*tert*-butanol solution (mixture C) and of the filtered MIL-88A(Fe) sample after 24 h of continuous stirring in mixture C.



	Residue (%) at 800 °C	MOF in membrane (%)
MIL-88A	33.9 %	81.9 %
PVDF	-	-
PVDF@MIL-88A-10%	5.06 %	12.2 %
PVDF@MIL-88A-20%	5.6 %	13.6 %
PVDF@MIL-88A-30%	11.7 %	28.3 %

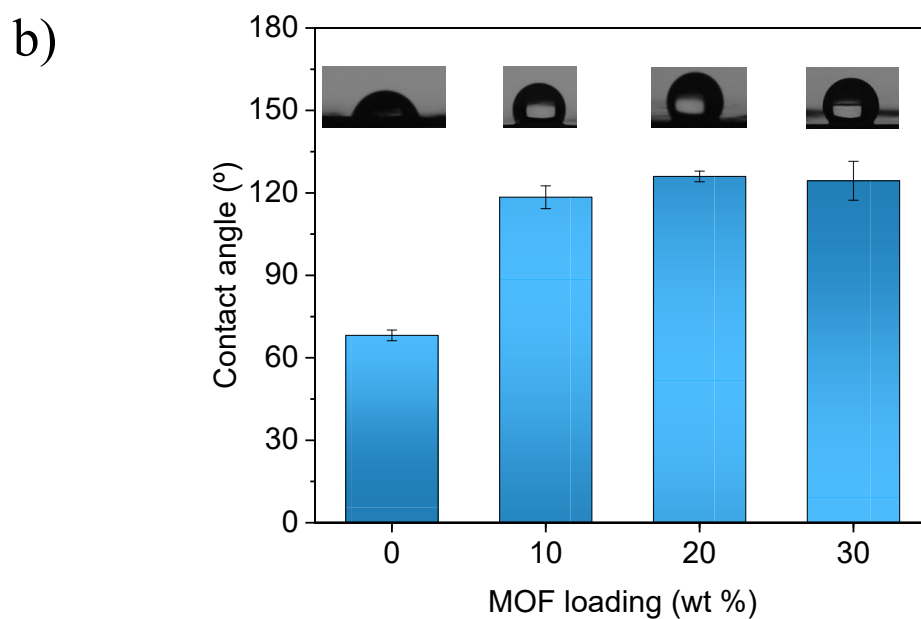


Figure S14. Membrane characterization: (a) TGA and (b) contact angle analysis.

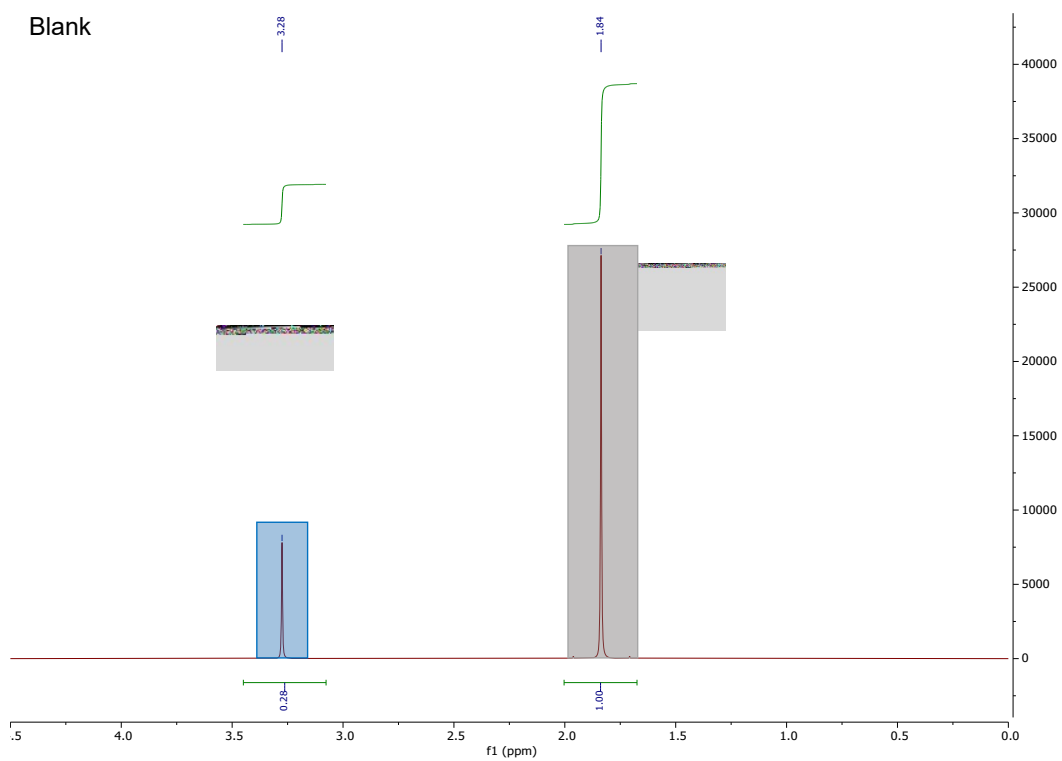


Figure S15. ^1H -NMR spectra of the blank methanol solution.

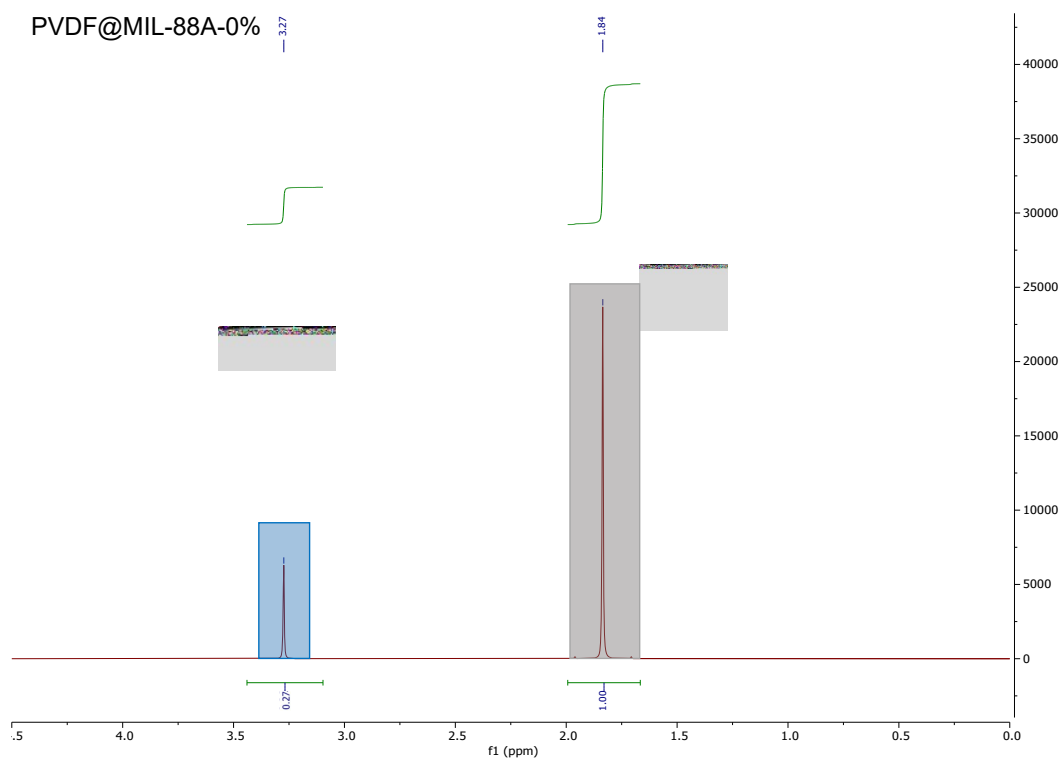


Figure S16. ^1H -NMR spectra of the filtered PVDF@MIL-88A-0% sample after 24 h of continuous stirring in methanol solution.

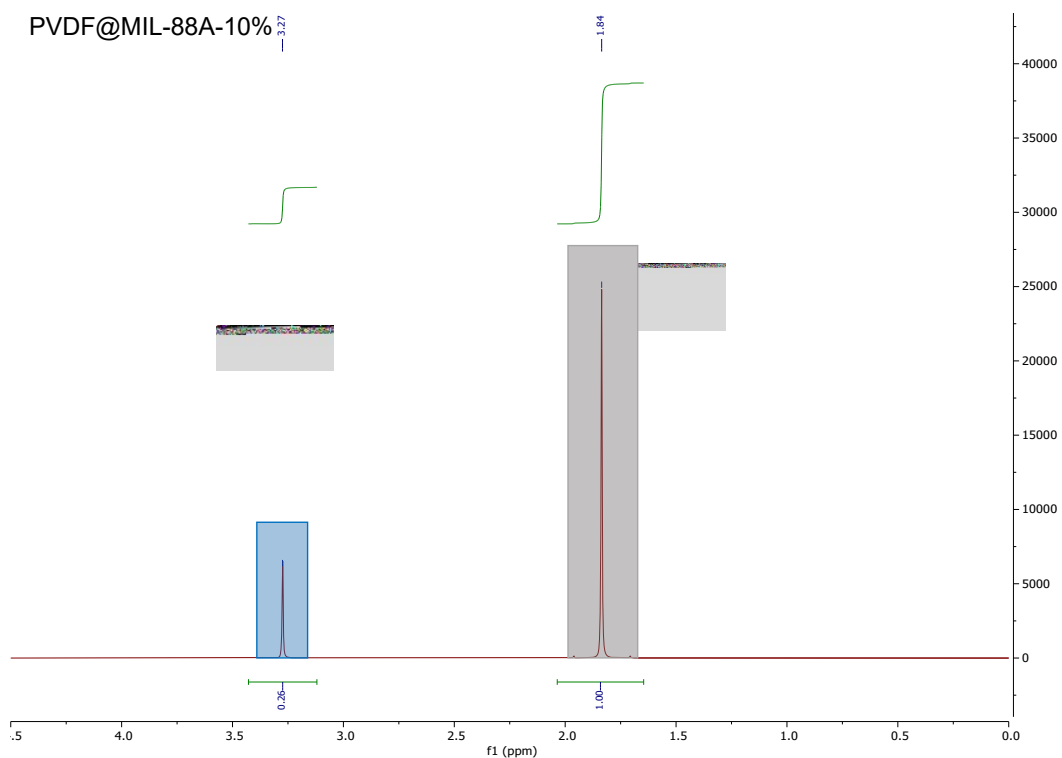


Figure S17. ^1H -NMR spectra of the filtered PVDF@MIL-88A-10% sample after 24 h of continuous stirring in methanol solution.

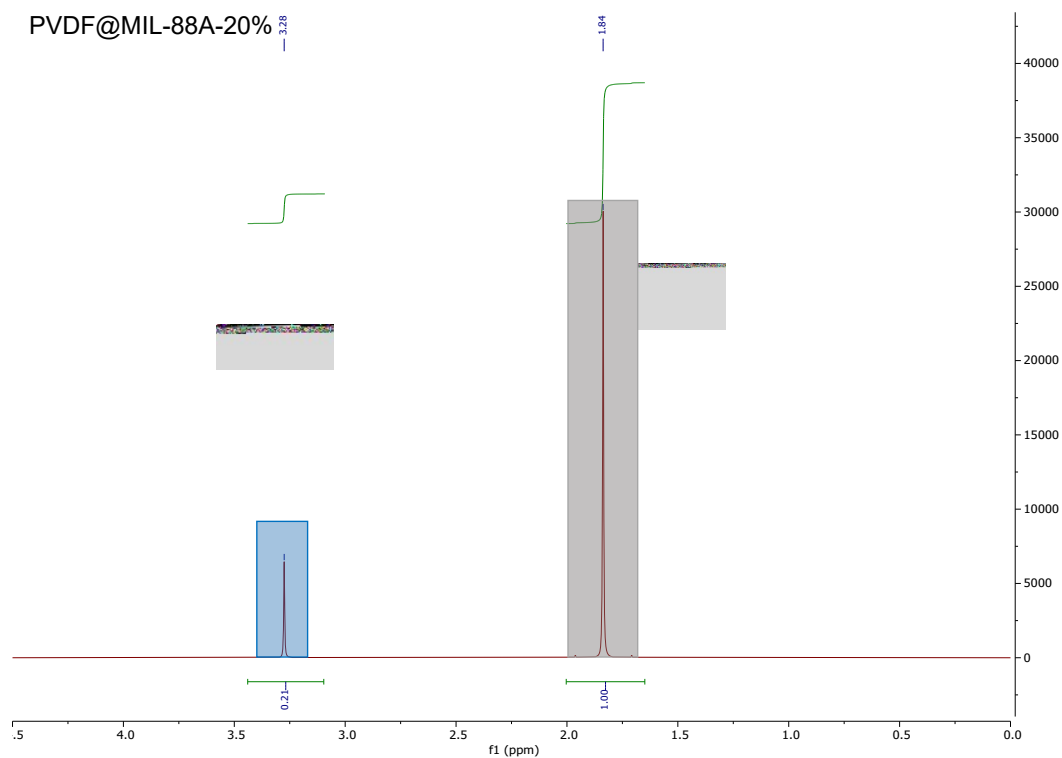


Figure S18. ^1H -NMR spectra of the filtered PVDF@MIL-88A-20% sample after 24 h of continuous stirring in methanol solution.

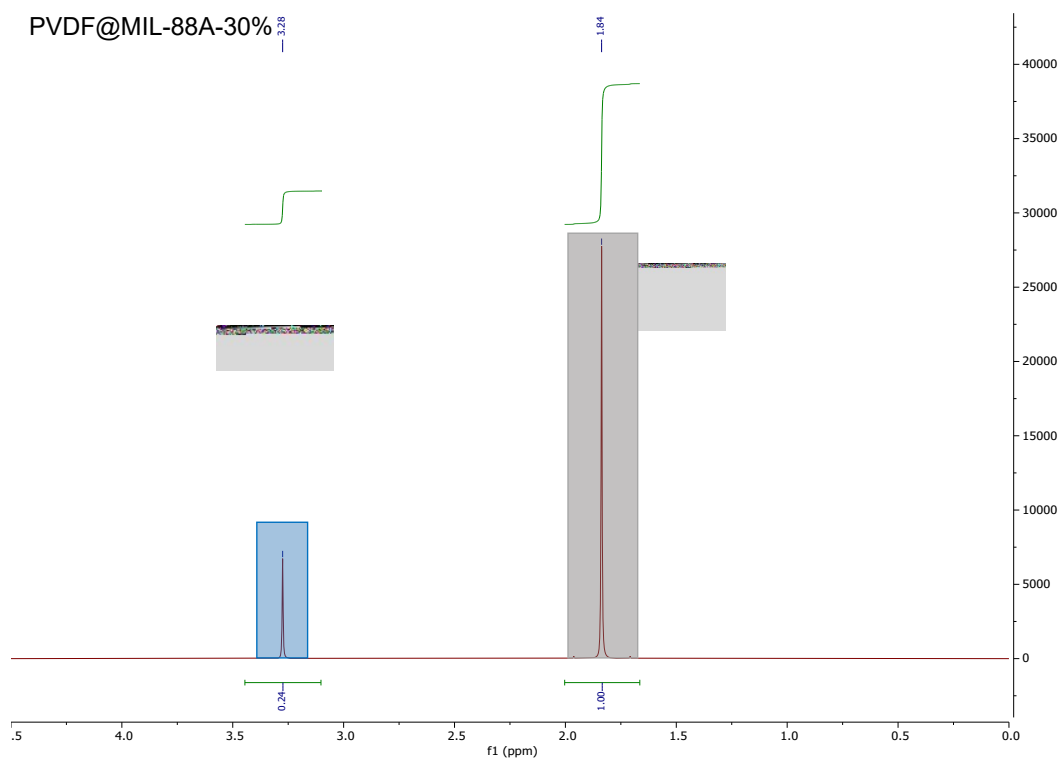


Figure S19. ^1H -NMR spectra of the filtered PVDF@MIL-88A-30% sample after 24 h of continuous stirring in methanol solution.

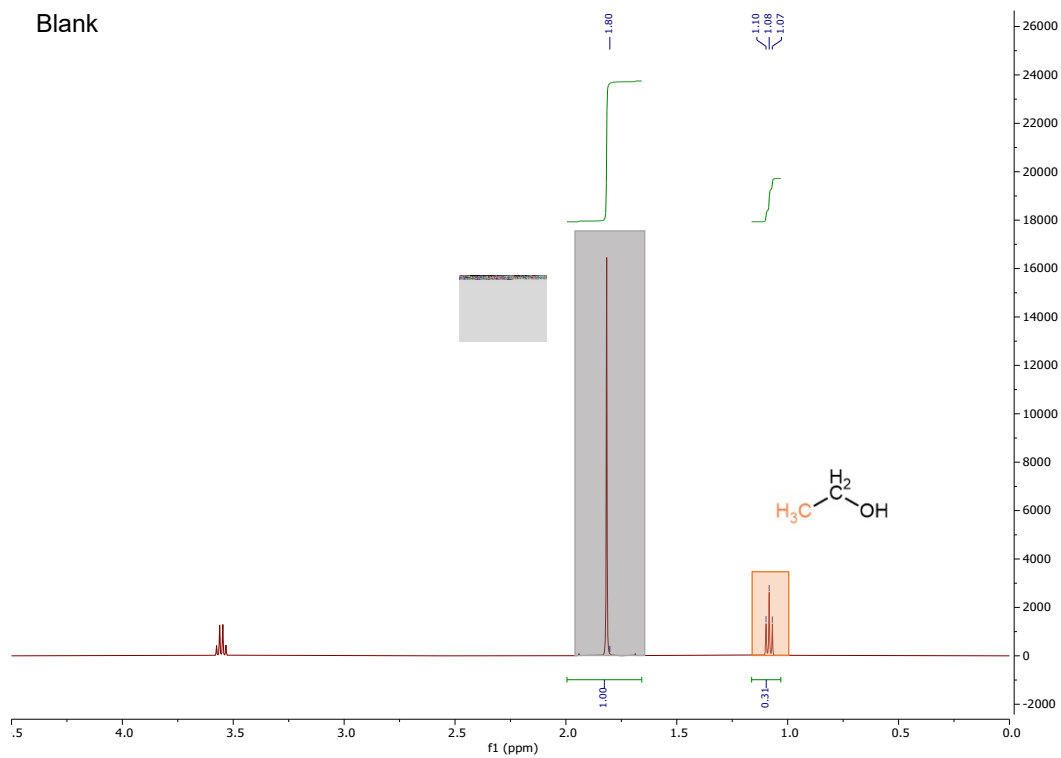


Figure S20. ^1H -NMR spectra of the blank ethanol solution.

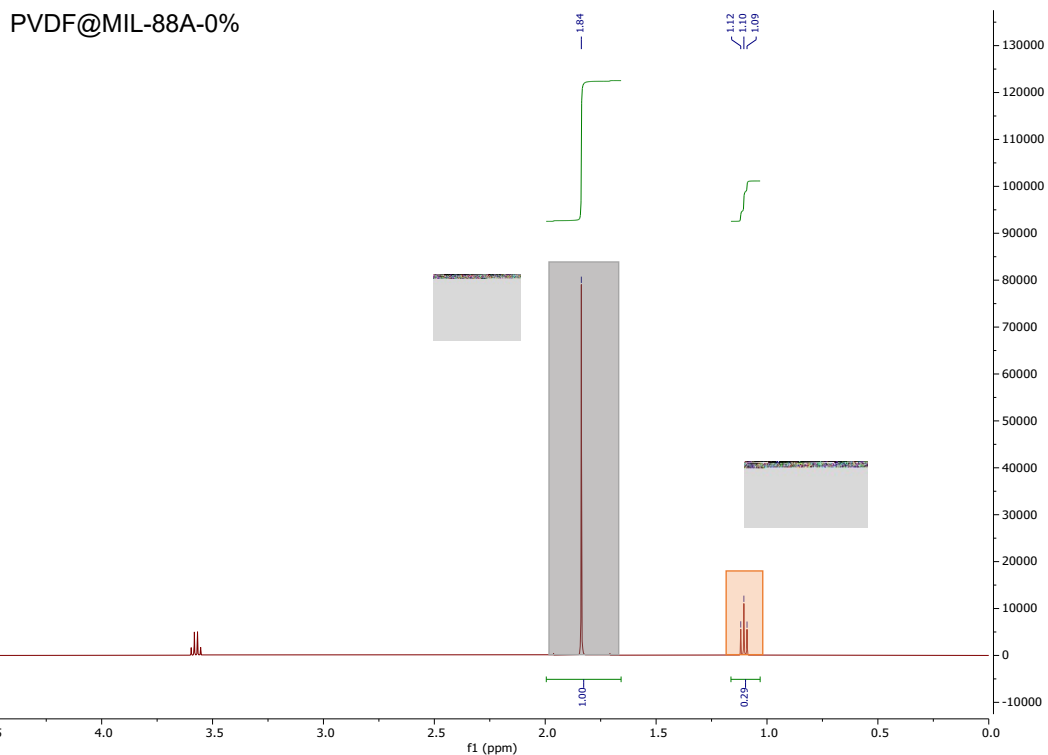


Figure S21. ^1H -NMR spectra of the filtered PVDF@MIL-88A-0% sample after 24 h of continuous stirring in ethanol solution.

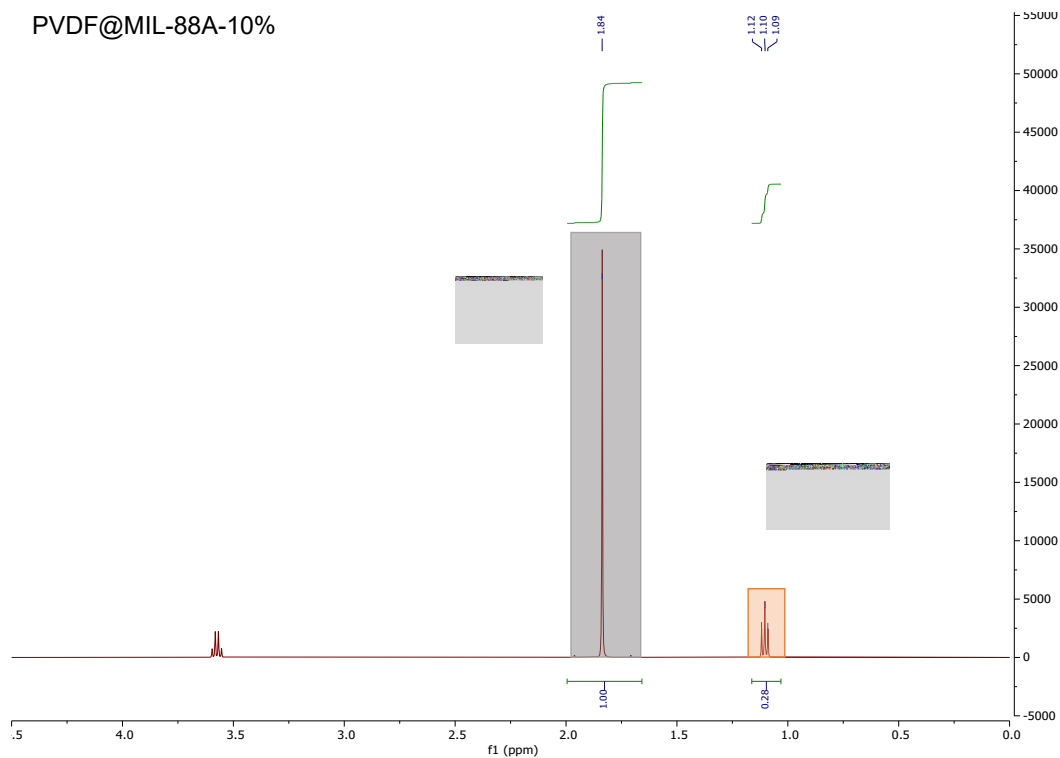


Figure S22. ^1H -NMR spectra of the filtered PVDF@MIL-88A-10% sample after 24 h of continuous stirring in ethanol solution.

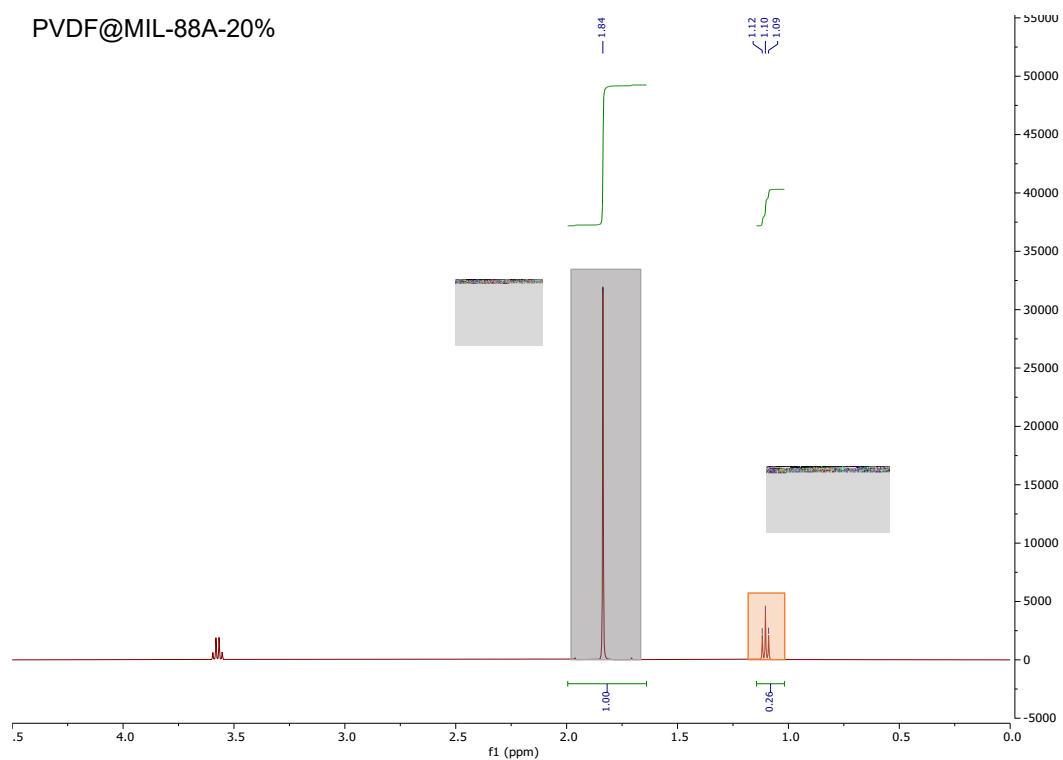


Figure S23. $^1\text{H-NMR}$ spectra of the filtered PVDF@MIL-88A-20% sample after 24 h of continuous stirring in ethanol solution.

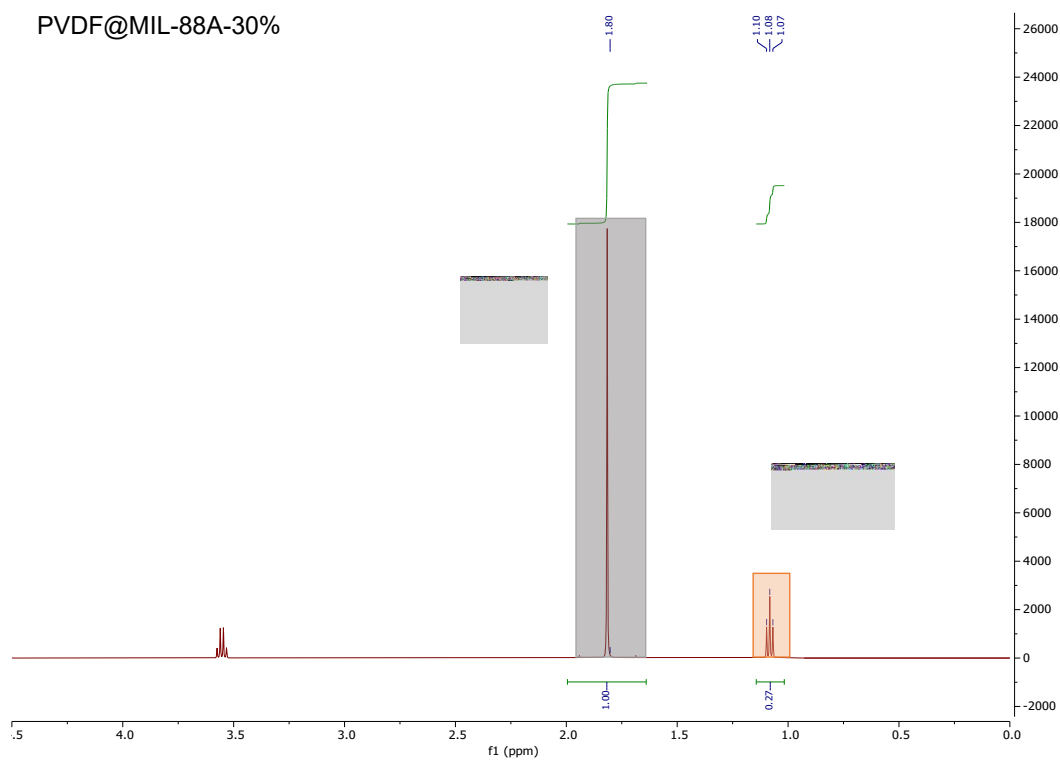


Figure S24. $^1\text{H-NMR}$ spectra of the filtered PVDF@MIL-88A-30% sample after 24 h of continuous stirring in ethanol solution.

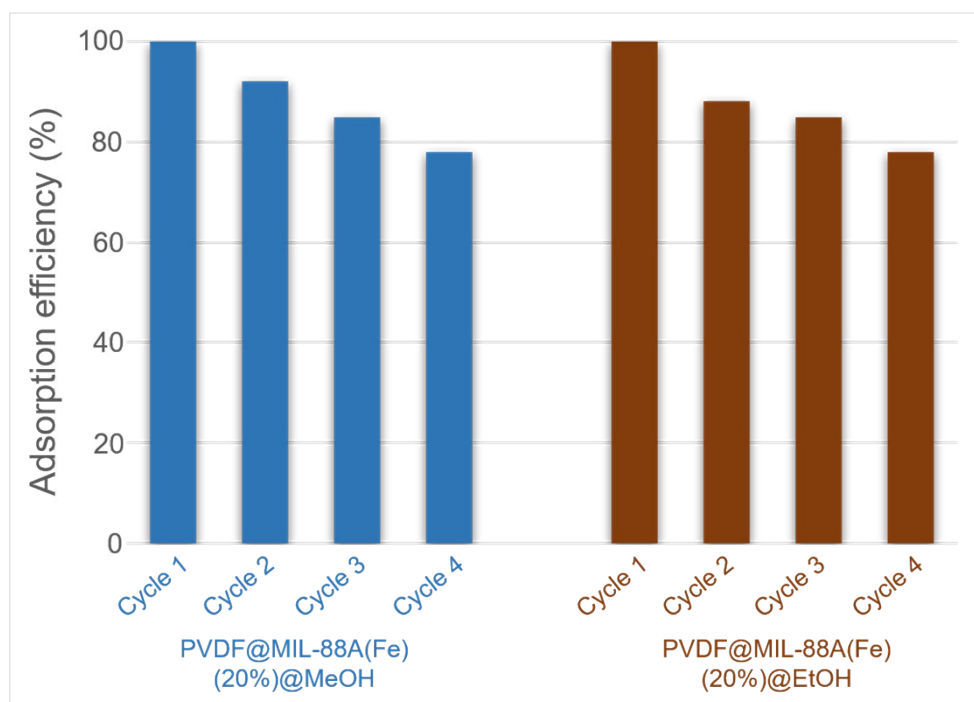


Figure S24. Recyclability performance of PVDF@MIL-88A(Fe) (20%) toward MeOH and EtOH capture from water.

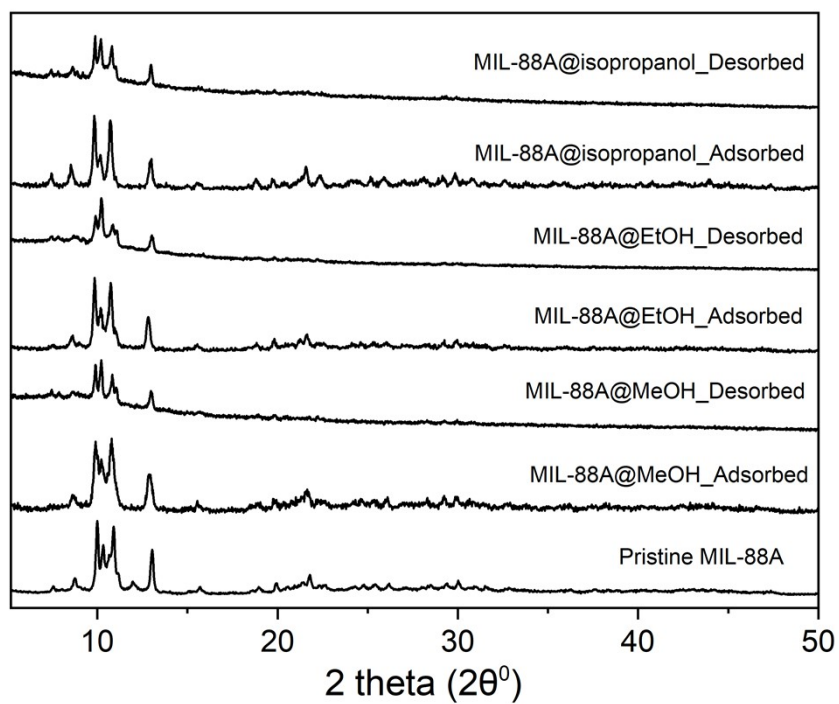


Figure S25. PXRD patterns of MIL-88A(Fe) before and after alcohol adsorption process for methanol, ethanol and isopropanol.

References:

1. L. Sarkisov, R. Bueno-Perez, M. Sutharson, D. Fairen-Jimenez, *Chem. Mater.* 2020, 32 (23), 9849–9867.
2. C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk, G. Férey, *Science* 2007, 315 (5820), 1828–1831.
3. Accelrys Inc. *Materials Studio*, 2011.
4. M. P. Allen, D. J. Tildesley, *Computer simulation of liquids*; Clarendon Press; Oxford University Press, 1987.
5. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, W. M. Skiff, *J. Am. Chem. Soc.* 1992, 114 (25), 10024–10035.
6. U. C. Singh, P. A. Kollman, *J. Comput. Chem.* 1984, 5 (2), 129–145.
7. B. Delley, *The Journal of Chemical Physics* 2000, 113 (18), 7756–7764.
8. B. Chen, J. J. Potoff, J. I. Siepmann, *J. Phys. Chem. B* 2001, 105 (15), 3093–3104.
9. N. Barroso, J. Andreo, G. Beobide, O. Castillo, A. Luque, S. Perez-Yáñez, S. Wuttke, *Commun. Chem.* 2023, 6 (4), 1-9. DOI: 10.1038/s42004-022-00799-w.