

-Supplementary info file-

Functionalized flexible MOF as filler in mixed matrix membranes for highly selective separation of CO₂ from CH₄ at elevated pressures

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1.- Experimental procedures

1.1.- NH₂-MIL-53 Synthesis. The NH₂-MIL-53(Al) microcrystals were synthesized by means of microwave irradiation. Aluminium chloride (AlCl₃·6H₂O, Fluka, purum p.a.), amino-terephthalic acid (Aldrich, 99%) were used as received. The reinforced Teflon microwave autoclaves were filled with a mixture containing 1.97 g of AlCl₃ and 1.5 g amino-terephthalic acid in 20 mL of deionized water. Synthesis was carried out during 30 min at 423 K using a power of 10 W/mL. The resulting yellow powder was filtered under vacuum and washed with acetone. The samples were activated in DMF at 423 K under hydrothermal conditions and stored at 373 K.

1.2.- MMM Fabrication. For the membrane preparation, PSF Udel P-3500 (kindly supplied by Solvay Advanced Polymers) was degassed at 373 K for 4 h under vacuum to remove adsorbed water. This amorphous high performance polymer has excellent thermal and mechanical properties, and presents good solubility in many solvents such as dichloromethane, chloroform, or tetrahydrofuran.

The first step was to fabricate the plain polymeric membrane for the purpose of comparison with those containing increased amounts of NH₂-MIL-53(Al). For the pure membrane, 0.4 g of PSF was dissolved in 3.6 mL of chloroform and stirred for 1 day, leading to a viscous solution. The fabrication procedure for the MMMs was identical to the pure polymer membrane preparation but with a previous dispersion stage of NH₂-MIL-53(Al) in the solvent (in a proportion of 90/10 wt.% solvent/filler-polymer mixture, maintained constant for all cases) for 15 min in an ultrasonic bath. PSF was then added, and the whole mixture was magnetically stirred for 1 day. Before the membrane casting three intervals of sonication for 15 min were carried out to ensure a well-dispersed solution. Subsequently, the homogeneous solution was poured on a flat glass plate and then left overnight partially closed to slow down the natural evaporation of solvent under ambient conditions. The last step was the vacuum treatment to remove the remaining solvent within the membrane. The treatment took place in a vacuum oven at 383 K. Membranes with different amounts of MOF charge (8, 16, 25, and 40 wt.%) were prepared with thicknesses around 75- 100 μm. Membrane areas of 4.4 cm² were cut from the films for permeation tests.

1.2.- Characterization Techniques

Scanning electron microscopy (SEM) on a Philips XL20 (15-30 kV) microscope was used to determine crystal morphology and size of the NH₂-MIL-53(Al) particles and MMMs. Membrane images were obtained by previous freeze fracturing after immersion in liquid nitrogen.

High-pressure adsorption isotherms of pure CO₂ (purity of 99.995%) in the powder and MMMs materials were determined by the volumetric technique (Belsorp HP) using 0.5 gram of sample. Before every measurement, the adsorbent was regenerated by increasing the temperature to 373 K at a rate of 10 K/min under vacuum and maintaining the temperature for 2 h.

Infrared spectra were recorded in a Bruker model IFS66 spectrometer in DRIFT mode on a high temperature cell with CaF₂ windows. The spectra were collected after accumulation of 128 scans with a resolution of 4 cm⁻¹. Before collecting the spectra, the sample was pretreated in the equipment under helium at 373 K for 1 h.

2.- Experimental results

2.1.- NH₂-MIL-53(Al) synthesis

Figure S-1 shows SEM micrographs of the NH₂-MIL-53(Al) synthesized under microwave irradiation. Homogeneous elongated particles of 0.2 x 1 μm can be observed.

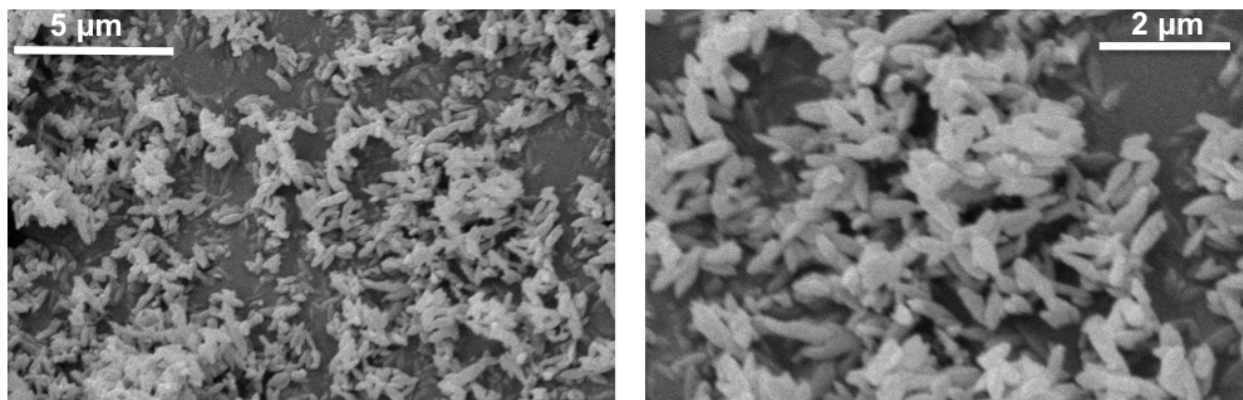


Figure S-1.- SEM micrographs of the NH₂-MIL-53(Al) synthesized under microwave irradiation

2.2.- High pressure adsorption isotherms

Figure S-2 shows the CO₂ adsorption isotherms measured on different membrane samples containing 0, 25 and 40 wt.% NH₂-MIL-53(Al). At low pressures the contribution of the MOF is almost negligible, most probably due to the low concentration of adsorbate at the polymer layer surrounding the microporous filler. In contrast, as the CO₂ pressure is increased, the contribution of the MOF to the total uptake becomes increasingly important and even breathing of the framework can be noticed.

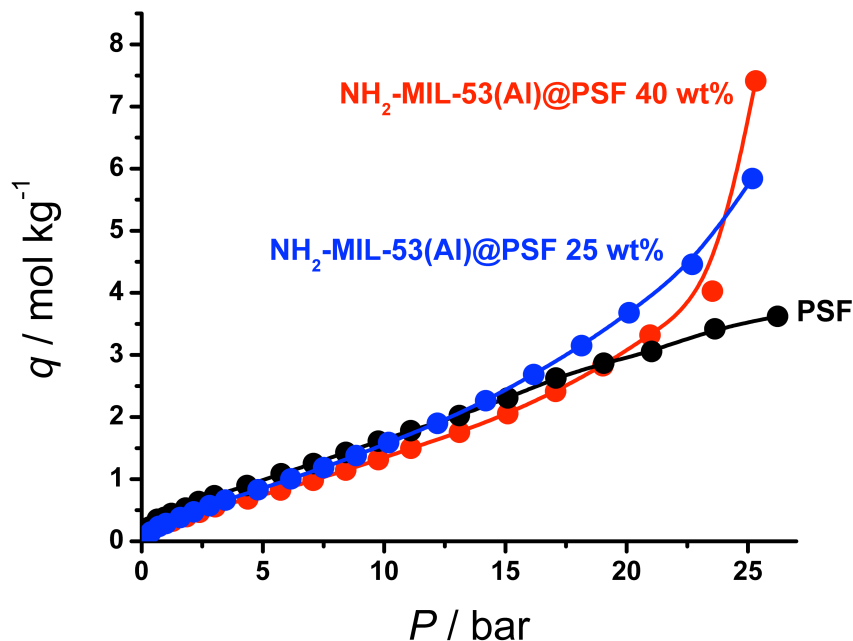


Figure S-2.- CO₂ adsorption isotherms measured on different MMM samples containing 0, 25 and 40 wt.% NH₂-MIL-53(Al) at 308 K

2.3.- DRIFTS

In figure S-3 the infrared spectra of pure NH₂-MIL-53, PSF and MMMs at different MOF loadings are depicted. When focusing on the NH₂-MIL-53(Al) sample, the broad band centred around 3680 cm⁻¹ along with a shoulder at 3693 cm⁻¹ are assigned to the bridging hydroxyl group of the MIL-53, i.e. Al-OH-Al.^[1] The shoulder position is very close to that reported for unfunctionalized MIL-53, while the main band is slightly shifted. We attribute the main band to hydroxyl groups which are directly interacting with the neighbouring amines (see below) while the shoulder at 3693 cm⁻¹ corresponds to surface -OH groups not engaged in hydrogen bonding. The two sharp bands at 3387 and 3498 cm⁻¹ in the spectra of samples containing NH₂-MIL-53(Al) are due to the symmetric and asymmetric vibrations of -NH₂ groups, respectively.^[2]

After inclusion in the polymer matrix, all main features from both the PSF and MOF can be observed, but a clear shift in both the -OH and -NH₂ bands of the MOF occurs. In the case of the OH stretching, the main band becomes broader and red-shifted to 3672 cm⁻¹, while the shoulder attributed to free OH groups at the surface disappears. At the same time, both symmetric and

asymmetric amine stretchings are slightly blue shifted. We attribute these effects to the formation of hydrogen bonds between MOF and polymer at their interface.

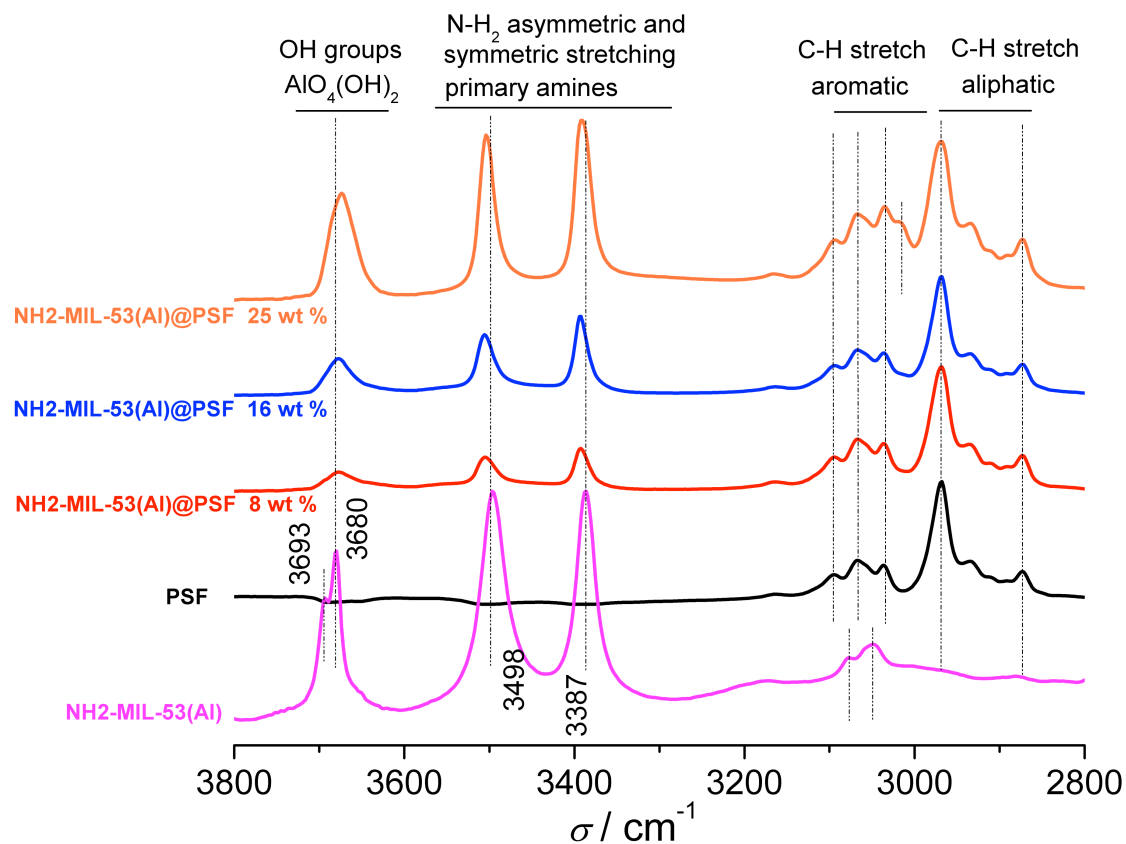


Figure S-3.- Infrared spectra of pure NH₂-MIL-53, PSF and MMMs at different MOF loadings

References

- [1] C. Volkringer, T. Loiseau, N. Guillou, G. Férey, E. Elkaim, A. Vimont, *Dalton Trans.* **2009**, 2241-2249.
- [2] E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon, F. Kapteijn, *Langmuir* **2011**, 27, 3970-3976.