Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Functionalized flexible MOF as filler in mixed matrix membranes for highly selective separation of CO_2 from CH_4 at elevated pressures

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Mixed matrix membranes (MMM) composed of a glassy polymer (Polysulfone) and the flexible metal organic framework NH_2-MIL-53(Al) exhibit excellent separation properties. High filler loadings, high dispersion and strong polymer-filler interaction have been achieved. In contrast to most reported membranes, CO_2/CH_4 separation performance increases with pressure, related to the flexibility of the filler.

Gas separation and purification based on membranes holds promise as energy efficient alternative to energy intensive distillation processes.[1] Separation through membranes is usually based on the size and the shape of the molecules to be separated or on their interaction with the membrane material.[2] In spite of the superior performance of membranes based on crystalline materials like zeolites[3] or metal organic frameworks (MOFs),[4] low flux polymeric membranes rule the commercial scene because of their easy processing and mechanical strength. Moreover, despite the important advances in the field, reproducibility and therefore scale up of pure zeolite- or MOF-based membranes is still a major issue.

During the last decades, several solutions have been proposed to boost the performance of polymeric membranes. Various polymers have been modified with inorganic fillers such as zeolites or mesoporous silicas to produce mixed matrix membranes (MMMs). [5-9] Although this approach has been shown to be successful in some cases, inorganic/polymer composite membranes often display void spaces between the filler and the polymeric matrix that allow molecules to bypass the filler particles, resulting in a loss of selectivity. [10, 11]

MOFs are attracting a lot of attention in the field of nanostructured materials. Next to a high surface area and pore volume, their chemical environment can be fine-tuned by selecting the appropriate building blocks[12] and/or by post-synthetic modification,[13] resulting in many design possibilities. When it comes to MMMs, the use of MOFs as fillers might result into a breakthrough in the field, since compatibility issues could eventually be overcome by optimizing the MOF linker-polymer interactions.

The incorporation of MOFs into a polymer matrix for gas separations was first explored by Won et al.[14] Since this pioneering work, only a few papers have been published on the topic.[15-23] Recently, Koros and co-workers reported the outstanding performance of ZIF-90@6FDA-DAM (6FDA: 2,2-bis (3,4-carboxyphenyl) hexafluoro- propane dianhydride, DAM: diaminomesitylene) MMMs.[18] In contrast to the MOFs used in the previous works, ZIF-90 contains a functional linker, imidazolate-2-carboxyaldehyde, that in combination with a highly permeable functionalized polymer, resulted in a good polymer-filler matching and therefore in an excellent separation performance.

In addition to the facile functionalization, and quite different from zeolites and other molecular sieve type materials, many MOFs are known to undergo structural changes upon adsorption of different molecules (‘breathing’).[24, 25] This striking property could, in principle, be used to manufacture MMMs resistant to solvents and eliminate plasticity behaviour, the most important structural drawbacks of polymeric membranes.

In this work we report the use of a breathing functionalized MOF as MMM filler. NH_2-MIL-53(Al) is a material based on the well-known MIL-53 topology [26] that presents excellent properties for the selective adsorption of CO_2.[27-30] Recently we discovered that the enhanced performance of the NH_2-MIL-53(Al) framework in CO_2 capture and separation is mostly due to its specific flexibility that results from a delicate interplay of weak dispersion forces controlling the flexibility of the framework. In contrast to its unfunctionalized counterpart, the narrow pore (*np*) form is preferred at low adsorbate pressures in the NH_2-MIL-53(Al). Only at high CO_2 partial pressures the framework expands to its large pore (*lp*) form.[30]

The microwave synthesized homogeneous, micron-sized NH_2-MIL-53(Al) particles (Figure S1) were used to fabricate nanocomposite membranes with PSF Udel® P-3500. To investigate the dispersion of the MOF within the polymer, cross-sectional micrographs of the MMMs containing 8, 16, 25 and 40 wt.% of NH_2-MIL-53(Al) (Figure 1) were examined by SEM.

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† Electronic Supplementary Information (ESI) available: experimental details and additional results. See DOI: 10.1039/b000000x/

The filler distribution is apparently homogeneous, and its presence is progressively more evident with increased loadings.

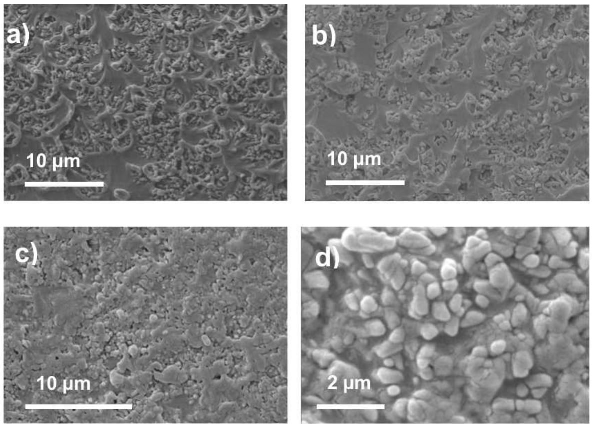

Figure 1. SEM micrographs of mixed matrix membrane cross-sections containing 8(a), 16(b), 25(c) and 40(d) wt.% NH_2-MIL-53(Al) crystals

Continuous MOF-polymer matrices are obtained at all loadings, even in the case of 40 wt.% (Figure 1d), an excellent polymer-MOF matching can be observed.

To unravel the effect of breathing on the adsorptive behavior of the composite, adsorption of CO_2 up to 25 bar has been studied on the different MMMs (Figure S-2) and compared with that of the pure MOF. In Figure 2 the contribution of the MOF to the total CO_2 uptake is plotted and compared with the adsorption isotherm of the pure NH_2-MIL-53(Al). At low pressures the contribution of the MOF is almost negligible, while as the CO_2 pressure is increased, the contribution of the MOF to the total uptake becomes more important and the rapid increase indicates even breathing of the framework, with a final total uptake similar to that the MOF filler in its *lp* form. In comparison with the bare material, the breathing is shifted to higher pressures, while the discrete adsorption steps have disappeared.

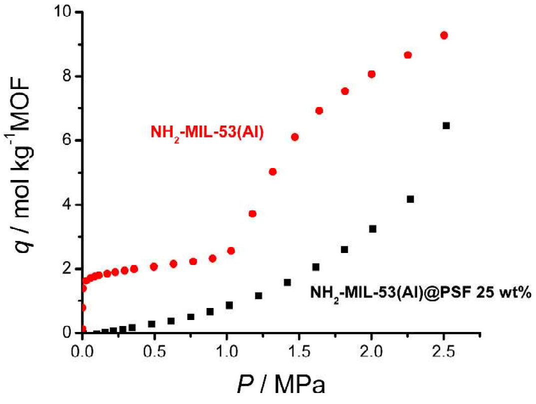

Figure 2. CO_2 uptake contribution of the MOF filler at 308 K in a NH_2-MIL-53(Al)@PSF 25 wt.% and the adsorption isotherm of pure NH_2-MIL-53(Al).

We attribute this effect to the external strain induced by the rigid polymer upon the embedded MOF particles, in line with recent experimental[31] and theoretical[32] studies on the effect of mechanical stress on flexible frameworks.

Figure 3 shows the CO_2 and CH_4 gas separation performance for a 1:1 mixture at 308 K and ΔP = 3 bar. Each type of membrane was fabricated and measured at least 3 times to provide reliable error estimates, which were always smaller than a 7 %. For loadings up to 25 wt.% the addition of NH_2-MIL-53(Al) produces a moderate CO_2 flow increase and a small decrease in CH_4 permeation that boost CO_2/CH_4 membrane selectivity by two-fold for the best performing membrane (25 wt.%). It is well known that in the case of MMMs an optimal filler loading exists. In the case of inorganic fillers like zeolites or silicas, due to the poor interaction filler-polymer, the optimal loading is always below a 10 wt.%. Considering that silica-based fillers have a higher density (about double) than that of a MOF, the volume fraction would be even higher. For MOF based MMMs, higher optimal loadings have been reported (~15 wt.%).[16-22] In the case of the amino functionalized framework-polysulfone couple, higher percentages of MOF can even be used without harming the membrane performance. We attribute this better matching to hydrogen bonding between the amine and sulphone groups of both constituents at their interface (see DRIFTS in supplementary information file, Figure S3). Indeed, similar hydrogen bonding interactions in various amino functionalized MOFs results in an easier shaping and, as we hypothesized, seem to have important consequences for the synthesis of MMMs.[33]

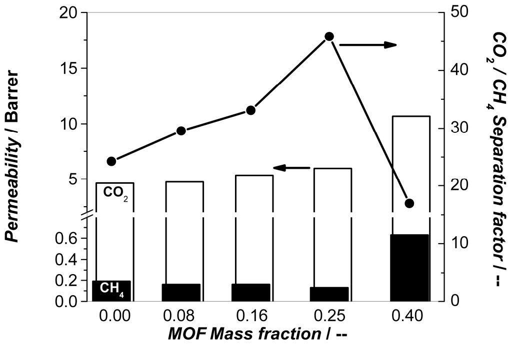

Figure 3. Separation performance of mixed matrix membranes with different MOF loadings at 308 K for a mixture CO_2:CH_4=1:1. p_{perm} = 1 bar, p_{ret} = 4 bar. CH_4 (black bars) and CO_2 (white bars) permeability (left *y*-axis) and CO_2/CH_4 separation factor (right *y*-axis). 1 Barrer = 3.348 x 10^{-19} kmol m / (m^2 s Pa).

Already at very low pressures, the presence of NH_2-MIL-53(Al) within the PSF matrix enhances the membrane separation performance. As the presented adsorption experiments indicate a very small contribution of the MOF at these low pressures, faster diffusion of CO_2 through the MOF crystals seems the cause of an enhanced membrane performance. To study the effect of the MOF filler at high adsorbate loadings together with the consequences of MOF flexibility, the high-pressure performance of the different MMMs was investigated. In order to reach high CO_2 loadings, experiments at reduced temperatures were performed. Separation results for CO_2:CH_4=1:1 mixtures at 263 K obtained for PSF and several MMMs containing a 8 and 25 wt.% MOF are presented in Figure 3.

The combination of high pressures and low temperatures has beneficial effects on the separation selectivity, since the CO_2

coverage is increased. Lower permeabilities are obtained due to a slower diffusion of both components (note that permeability is corrected by the pressure difference over the membrane). Interestingly, while for the pure polymer membrane the CO_2 selectivity reaches a maximum (≈55) at moderate pressures (5 bar), [10,11] in the case of the MOF containing MMMs, selectivities up to 110 are obtained at elevated pressures. By addition of MOF, a performance similar to the best polymeric membranes and selectivities 10 times higher than those reported to date for any pure MOF membrane for this separation are obtained. [34-36]

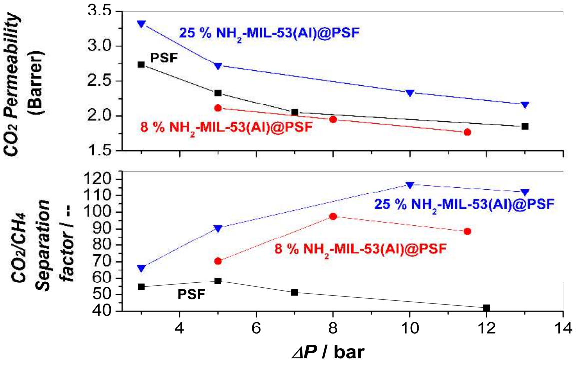

Figure 4. Separation performance of different mixed matrix membranes for a mixture CO_2:CH_4=1:1 as a function of the transmembrane pressure difference at 263 K (p_{perm} = 1 bar).

This increase in selectivity with pressure, opposite to the behaviour shown by most inorganic membranes, where this is an intrinsic property [37-40] or due to the presence of small defects that become more important at high pressures,[29,41] has very important consequences for applications like natural gas and biogas upgrading, where the retentate has to be kept pressurized. We speculate that the increase of selectivity is due to the intrinsic flexibility of the MOF filler: as pressure increases, adsorption in the CO_2 shape selective microporous MOF becomes more important (see Figures 2 and S2). Under the conditions plotted in Figure 4, the transition *np* → *lp* happens at ca. 5 bar of CO_2, when the performance of the pure polymeric membrane starts decaying. At this point, the expansion of the MOF particles might not only fill the gap between polymer chains due to the high CO_2 loading ('self healing' effect) but also contributes substantially to the total flux through the membrane. As result, higher fluxes and much better selectivities are obtained.

Summarizing, nanosized NH_2-MIL-53(Al) crystals with a narrow size distribution were synthesized by microwave heating. The NH_2-MIL-53(Al) particles showed an excellent adhesion with the polysulfone Udel® polymer in mixed matrix membranes without any additional compatibilization: high filler loadings are possible thanks to hydrogen bonding interactions between the MOF and the polymer. Mixed matrix membranes containing NH_2-MIL-53(Al) display a high performance for CO_2/CH_4 separation, while the use of flexible MOFs enhances the performance of the membrane at high pressures.

Universidad de Zaragoza gratefully acknowledges financial support from the Spanish Ministry of Science and Innovation (MAT2010-15870 and FPU Program). J.G. gratefully acknowledges the Dutch National Science Foundation (NWO-CW VENI) for financial support.

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-Supplementary info file-

Functionalized flexible MOF as filler in mixed matrix membranes for highly selective separation of CO_2 from CH_4 at elevated pressures

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1.- Experimental procedures

1.1.- NH_2-MIL-53 Synthesis. The NH_2-MIL-53(Al) microcrystals were synthesized by means of microwave irradiation. Aluminium chloride ($AlCl_3 \cdot 6H_2O$, 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 $AlCl_3$ 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 NH_2-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 NH_2-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 cm^2 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 NH_2-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 CO_2 (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 CaF_2 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.- NH_2-MIL-53(Al) synthesis

Figure S-1 shows SEM micrographs of the NH_2-MIL-53(Al) synthesized under microwave irradiation. Homogeneous elongated particles of 0.2 x 1 μm can be observed.

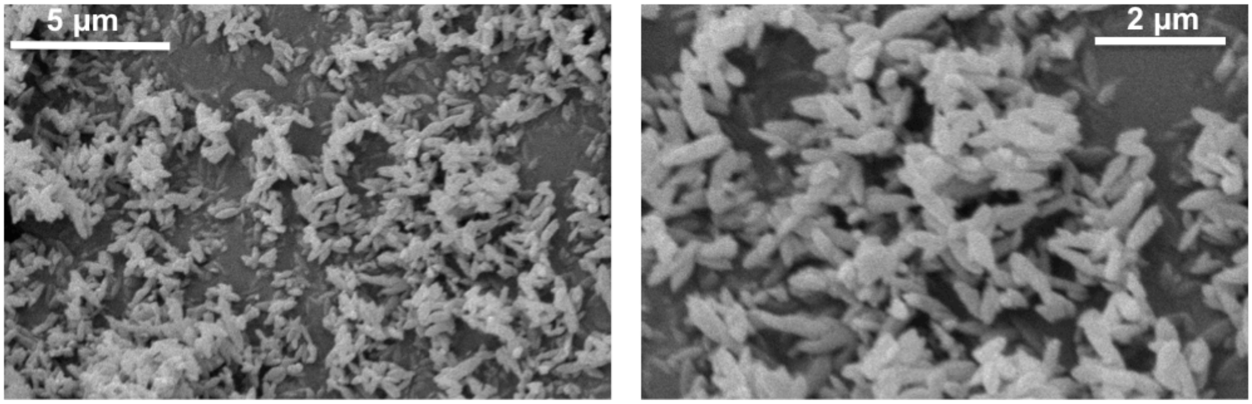

Figure S-1.- SEM micrographs of the NH_2-MIL-53(Al) synthesized under microwave irradiation

2.2.- High pressure adsorption isotherms

Figure S-2 shows the CO_2 adsorption isotherms measured on different membrane samples containing 0, 25 and 40 wt.% NH_2-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 CO_2 pressure is increased, the contribution of the MOF to the total uptake becomes increasingly important and even breathing of the framework can be noticed.

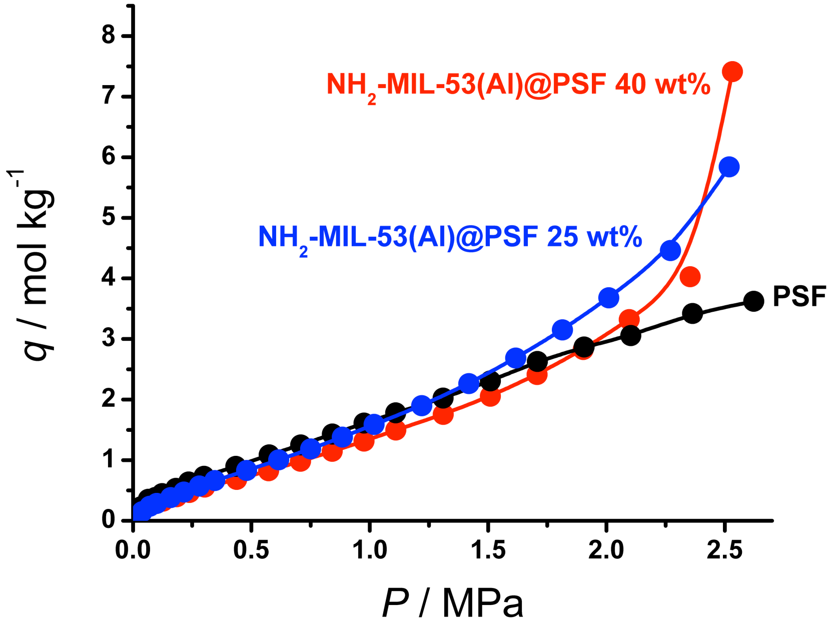

Figure S-2.- CO_2 adsorption isotherms measured on different MMM samples containing 0, 25 and 40 wt.% NH_2-MIL-53(Al) at 308 K

2.3.- DRIFTS

In figure S-3 the infrared spectra of pure NH_2-MIL-53, PSF and MMMs at different MOF loadings are depicted. When focusing on the NH_2-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 NH_2-MIL-53(Al) are due to the symmetric and asymmetric vibrations of -NH_2 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 -NH_2 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.

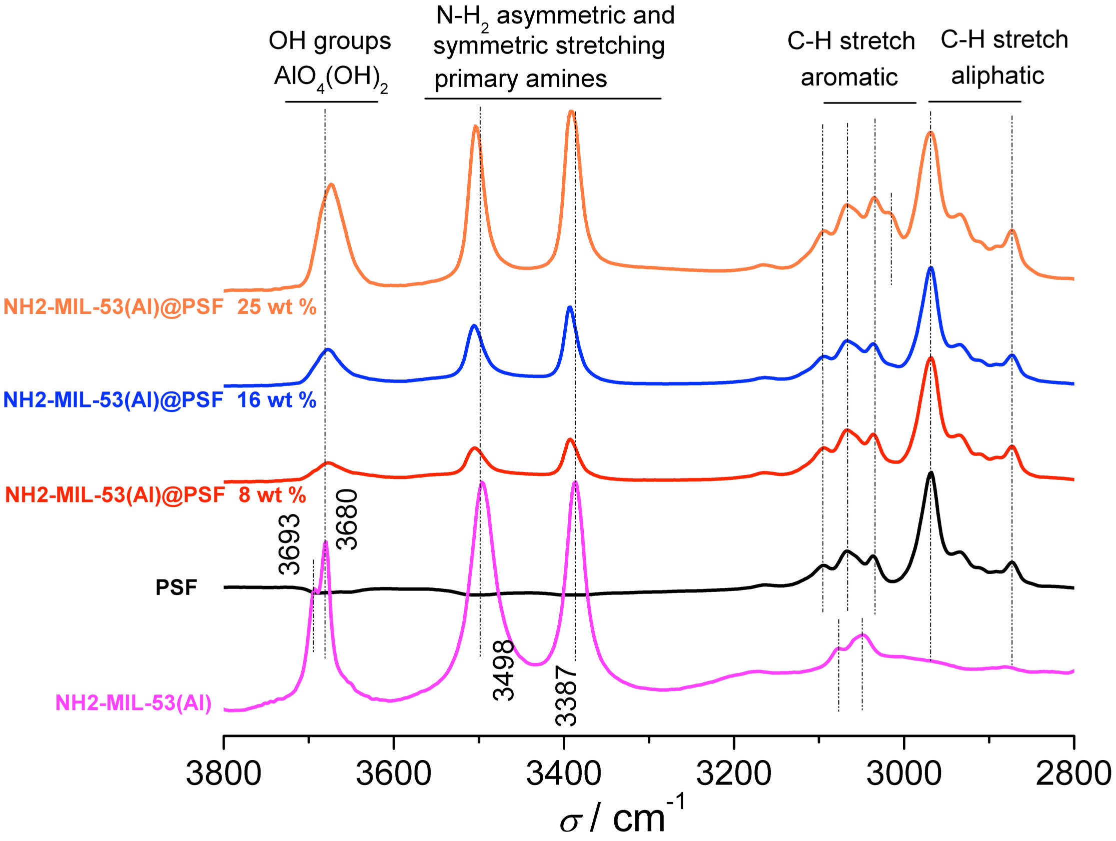

Figure S-3.- Infrared spectra of pure NH_2-MIL-53, PSF and MMMs at different MOF loadings

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