## Supporting Information

## Fabrication of MIL-120 membranes supported by a-Al<sub>2</sub>O<sub>3</sub>

## Hollow ceramic fibers for H<sub>2</sub> separation

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Fig.S1 XRD patterns of simulated (a) MIL-118; (b) MIL-121; (c) MIL-120; and (d) F-03.



Fig.S2 XRD patterns of simulated (a) MIL-118; (b) MIL-121; (c) MIL-120; (d) HCF; (e) F-03; (f) F-07; (g) F-08.

Gas(H <sub>2</sub> /j)	Knudsen constant	Temperature (K)	Single gas			Binary gas		
			Permeances	Permeances	Ideal separation	Permeances	Permeances	Separation
			(H <sub>2</sub> )	(j)	factor	(H <sub>2</sub> )	(j)	factor
H <sub>2</sub> /CH <sub>4</sub>	2.8	293	3.80×10 <sup>-7</sup>	4.9×10 <sup>-8</sup>	7.7	3.50×10 <sup>-7</sup>	4.43×10 <sup>-8</sup>	7.9
		313	5.0×10 <sup>-7</sup>	7.9×10 <sup>-8</sup>	6.3	4.36×10 <sup>-7</sup>	$7.30 \times 10^{-8}$	6.0
		343	5.86×10 <sup>-7</sup>	1.14×10 <sup>-7</sup>	5.1	5.0×10 <sup>-7</sup>	$1.00 \times 10^{-7}$	5.0
$H_2/N_2$	3.7	293	3.80×10 <sup>-7</sup>	5.14×10 <sup>-8</sup>	7.4	3.47×10 <sup>-7</sup>	4.75×10 <sup>-8</sup>	7.3
		313	5.0×10 <sup>-7</sup>	8.33×10 <sup>-8</sup>	6.0	4.21×10 <sup>-7</sup>	6.90×10 <sup>-8</sup>	6.1
		343	5.86×10 <sup>-7</sup>	1.30×10 <sup>-7</sup>	4.5	$4.74 \times 10^{-7}$	$1.05 \times 10^{-7}$	4.5
$H_2/CO_2$	4.7	293	3.80×10 <sup>-7</sup>	4.13×10 <sup>-8</sup>	9.2	3.58×10 <sup>-7</sup>	3.8×10 <sup>-8</sup>	9.4
		313	5.0×10 <sup>-7</sup>	6.80×10 <sup>-8</sup>	7.3	4.27×10 <sup>-7</sup>	5.90×10 <sup>-8</sup>	7.2
		343	5.86×10 <sup>-7</sup>	9.16×10 <sup>-8</sup>	6.4	$4.52 \times 10^{-7}$	$7.00 \times 10^{-8}$	6.4

Table.S1 Single and binary gas permeances (mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>) and separation factors for the MIL-120 membrane at 293K, 313K, 343K and 1 bar. The volume ratio for binary gas systems is 1:1.



Fig.S3 TG curve of the MIL-120 membrane (F-07) (under air, heating rate:  $1^{\circ}C \cdot min^{-1}$ ).



Fig.S4 (a)  $H_2/CO_2$ , (b)  $H_2/CH_4$  and (c)  $H_2/N_2$  permeances and separation factors of the MIL-120 membrane as a function of the permeation temperature at a pressure drop of 1bar (inverted triangles:  $CO_2$ , triangles:  $N_2$ , circles:  $CH_4$ , rhombuses:  $H_2$ , squares: separation factor).



Fig.S5 Differential enthalpies of adsorption and isotherm obtained with (a) nitrogen at 77 K, (b) hydrogen at 77 K on MIL-120, (c) Isotherms and (d) differential enthalpies of adsorption at 303 K obtained with carbon dioxide and methane on MIL-120<sup>1</sup>.

## Reference

 C. Volkringer, T. Loiseau, M. Haouas, F. Taulelle, D. Popov, M. Burghammer, C. Riekel, C. Zlotea, F. Cuevas and M. Latroche, *Chemistry of Materials*, 2009, **21**, 5783-5791.