Suplementary Materials

Post-hybridization of MIL-101(Cr) with graphene oxide enhances its hydrogen storage and release capacities

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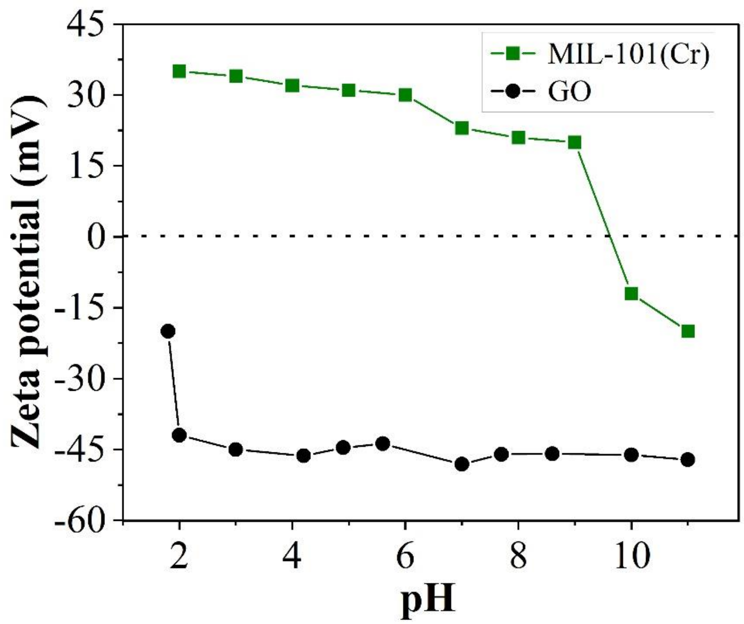

Figure S1: Zeta potential as a function of pH for pure Graphene Oxide (GO) and pure MIL-101(Cr).

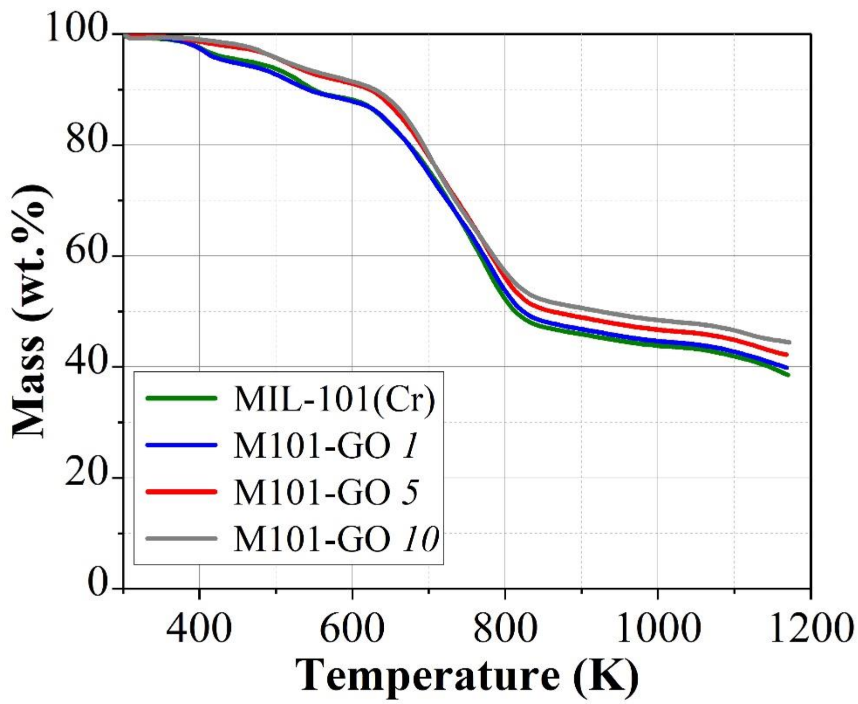

Figure S2: Thermogravimetric analysis (TGA, wt.%) of the pure MIL-101(Cr) and its hybrid materials.

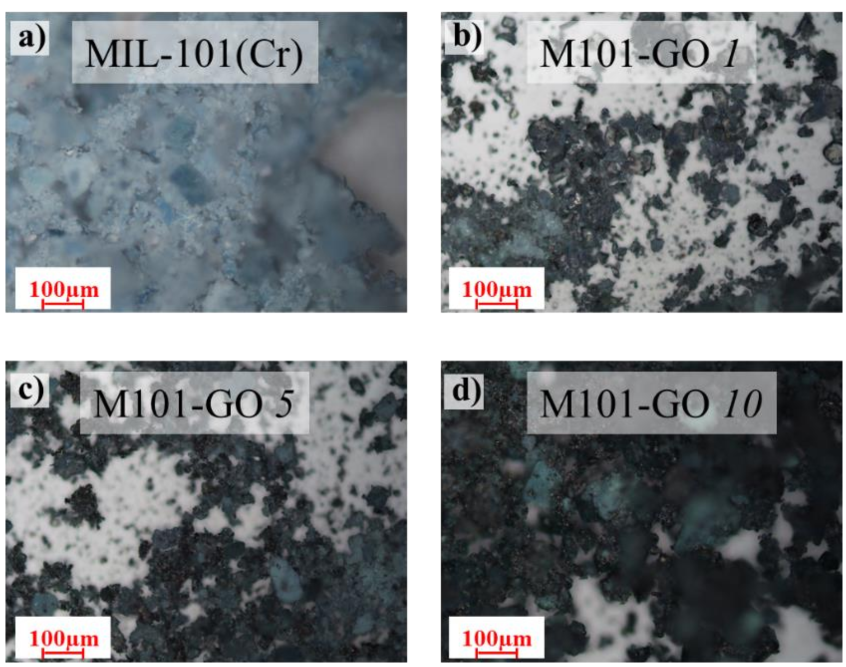

Figure S3: Optical microscopy images: a) MIL-101(Cr); b) M101-GO *1*; c) M101-GO *5* and d) M101-GO *10*.

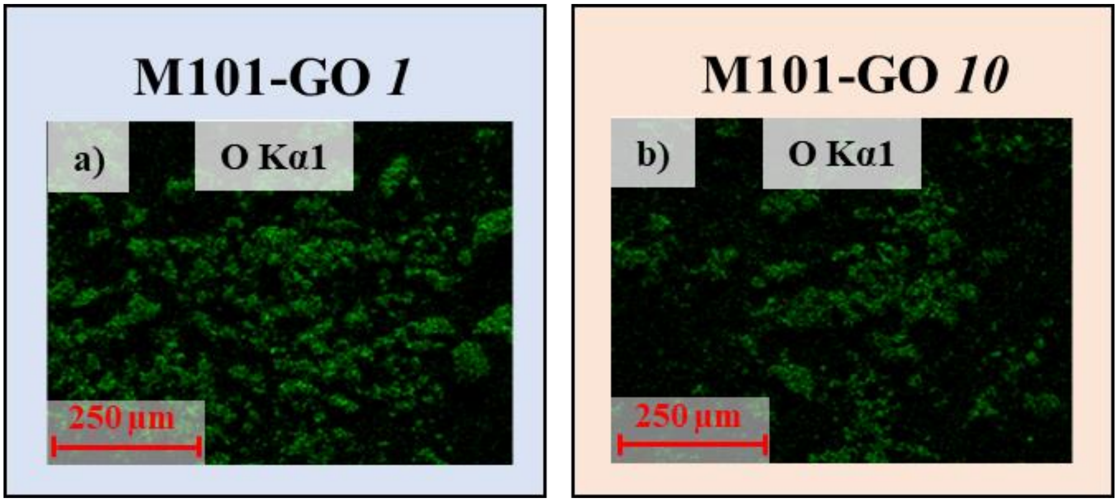

Figure S4: Oxygen (O) mapping by SEM-EDX of: a) M101-GO *1* and b) M101-GO *10*.

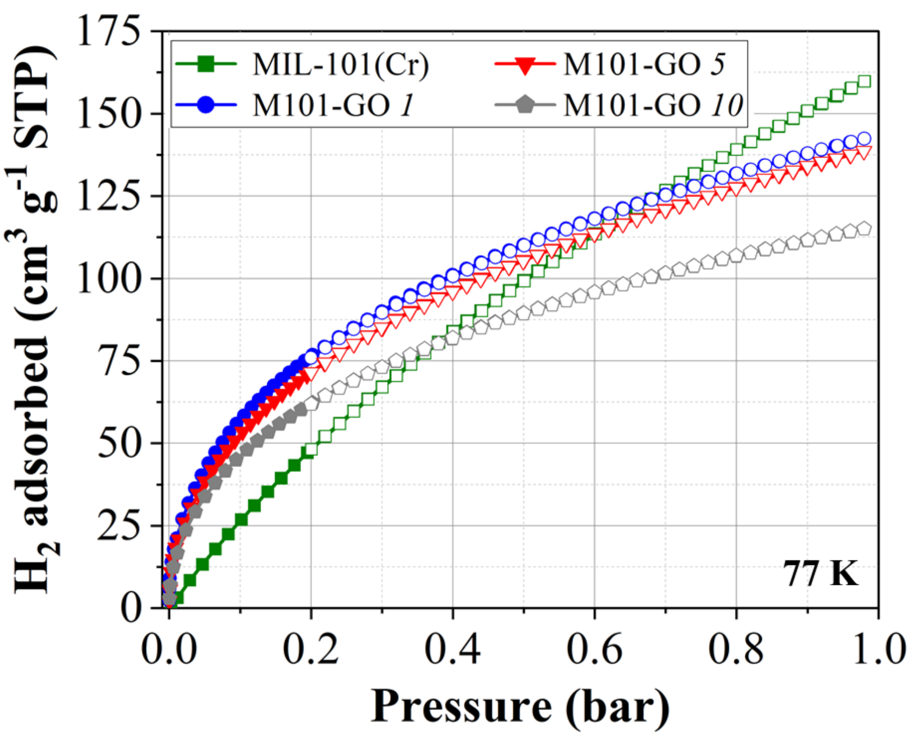

Figure S5: H_2 adsorption-desorption isotherms for pure MIL-101(Cr) and its hybrids.

Table S1: Textural properties of the pure MIL-101(Cr) and hybrid materials.

Method	Parameter	MIL-101(Cr)	M101-GO *1*	M101-GO *5*	M101-GO *10*
BET	$A_{BET\ N2}$ ($m^2\ g^{-1}$)	2370	1740	1670	1400
	$A_{BET\ Ar}$ ($m^2\ g^{-1}$)	2010	1640	1475	1225
V_T at p/p°=0.97	$V_{T\ N2}$ ($cm^3\ g^{-1}$)	2.44	1.39	1.28	0.98
	$V_{T\ AR}$ ($cm^3\ g^{-1}$)	2.12	1.23	1.14	0.85
2D-NLDFT N_2 and H_2 at 77 K	$S_{2D\text{-}NLDFT}$ ($m^2\ g^{-1}$)	1465	1240	1180	970
	$V_{T2D\text{-}NLDFT}$ ($cm^3\ g^{-1}$)	2.23	1.31	1.20	0.92
	V_{meso} ($cm^3\ g^{-1}$)	1.54	0.72	0.65	0.47
	V_{μ} ($cm^3\ g^{-1}$)	0.69	0.59	0.55	0.45
	$V_{s\mu}$ ($cm^3\ g^{-1}$)	0.69	0.54	0.50	0.39
	$V_{u\mu}$ ($cm^3\ g^{-1}$)	0.00	0.05	0.05	0.06
Density	ρ_{tap} ($kg\ m^{-3}$)	259	285	290	302
	ρ_{sk} ($kg\ m^{-3}$)	2155	1884	1891	1906

The surface area, A_{BET}, was determined using the BET equation applied to the adsorption isotherms of nitrogen and argon. Total pore volumes, V_{TN2} and V_{TAr}, were calculated from the isotherms at p/p°=0.97. The 2D-NLDFT-HS model, developed for heterogeneous carbon surfaces, was applied to N_2 and H_2 adsorption isotherms at 77 K.

Table S2: Excess H_2 uptake (wt.%), total H_2 uptake (wt.% and kg m^{-3}) and release capacity (kg m^{-3}) for the pure MOF and hybrid materials.

Method	Parameter	MIL-101(Cr)	M101-GO *1*	M101-GO *5*	M101-GO *10*
Excess H_2 uptake (wt.%)	77K; 40 bars	3.78	3.65	3.00	2.43
	160K; 100 bars	2.53	2.86	2.60	2.20
	273K; 100 bars	0.55	0.77	0.64	0.59
Excess H_2 uptake (kg m^{-3})*	160K; 100 bars	6.55	8.15	7.54	6.64
	273K; 100 bars	1.42	2.19	1.86	1.78
Total H_2 uptake (kg m^{-3})	77K; 100 bars	33.83	35.80	33.63	31.88
	77K; 5 bars	7.09	8.16	6.96	6.11
	160K; 5 bars	1.33	1.64	1.11	2.61
Release capacity (kg m^{-3})	$R^{77K\rightarrow77K}$	26.74	27.64	26.67	25.77
	$R^{77K\rightarrow160K}$	32.50	34.16	32.25	29.27

*Excess H_2 uptake (kg m^{-3}) was calculated by multiplying the n_{exc} (wt.%) by the ρ_{tap} (kg m^{-3}).

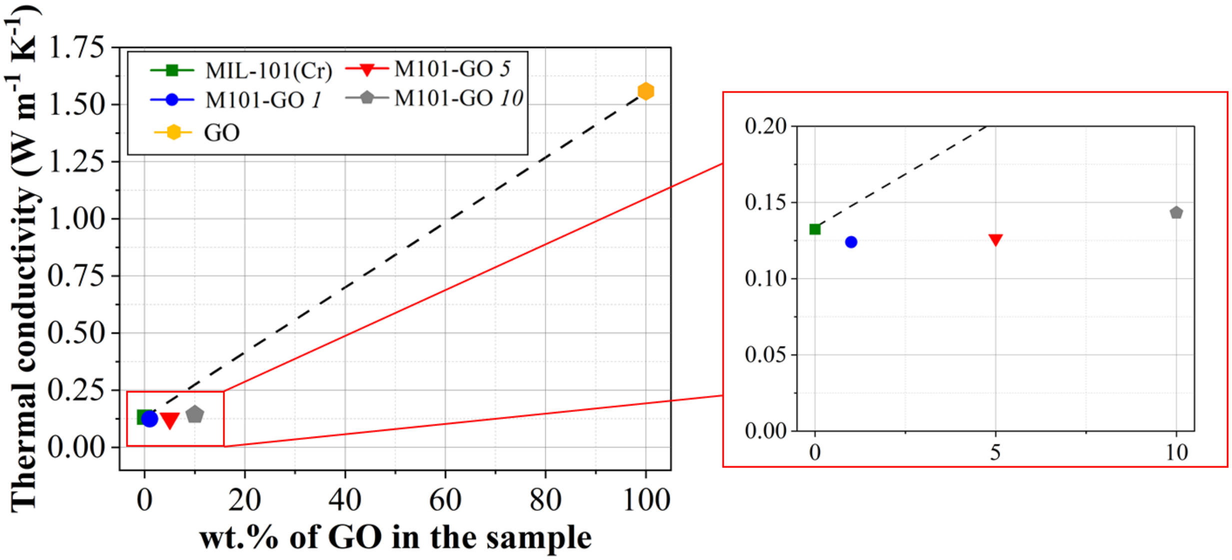

Figure S6: Thermal conductivity of the samples measured in powder form (298 K and 25% relative humidity).

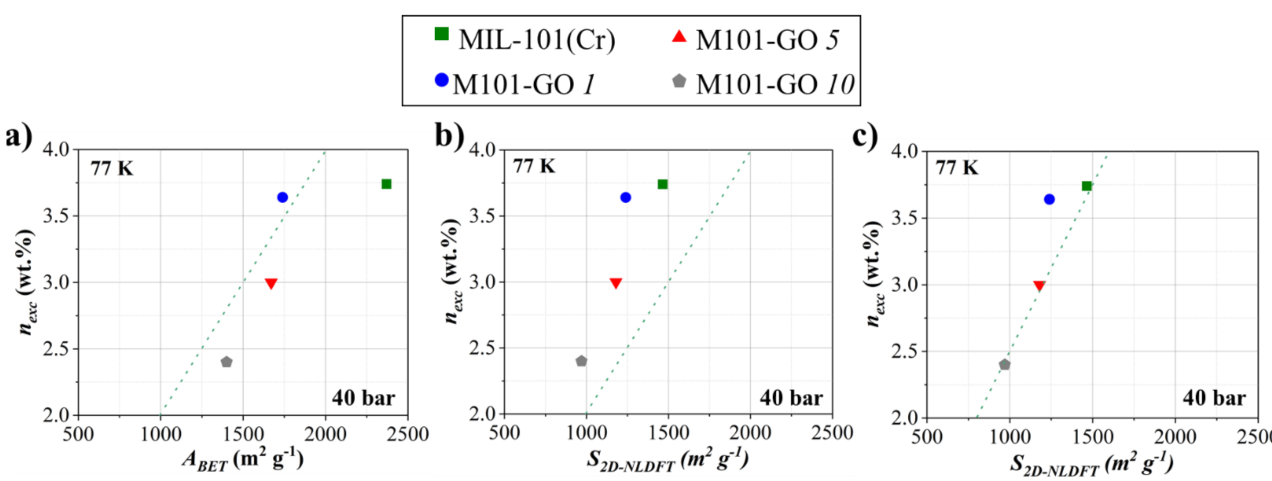

Figure S7: n_{exc} as a function of materials' surface area measured at 77 K and 40 bars: a) Chahine's rule for pure MIL-101(Cr) and hybrids as a function of A_{BET}; b) Same as a) but as a function of $S_{2D\text{-}NLDFT}$; c) n_{exc} (wt.%) of pure MIL-101(Cr) and hybrids as a function of the $S_{2D\text{-}NLDFT}$ with a progression of 1.25 wt.% for each 500 $m^2\ g^{-1}$.

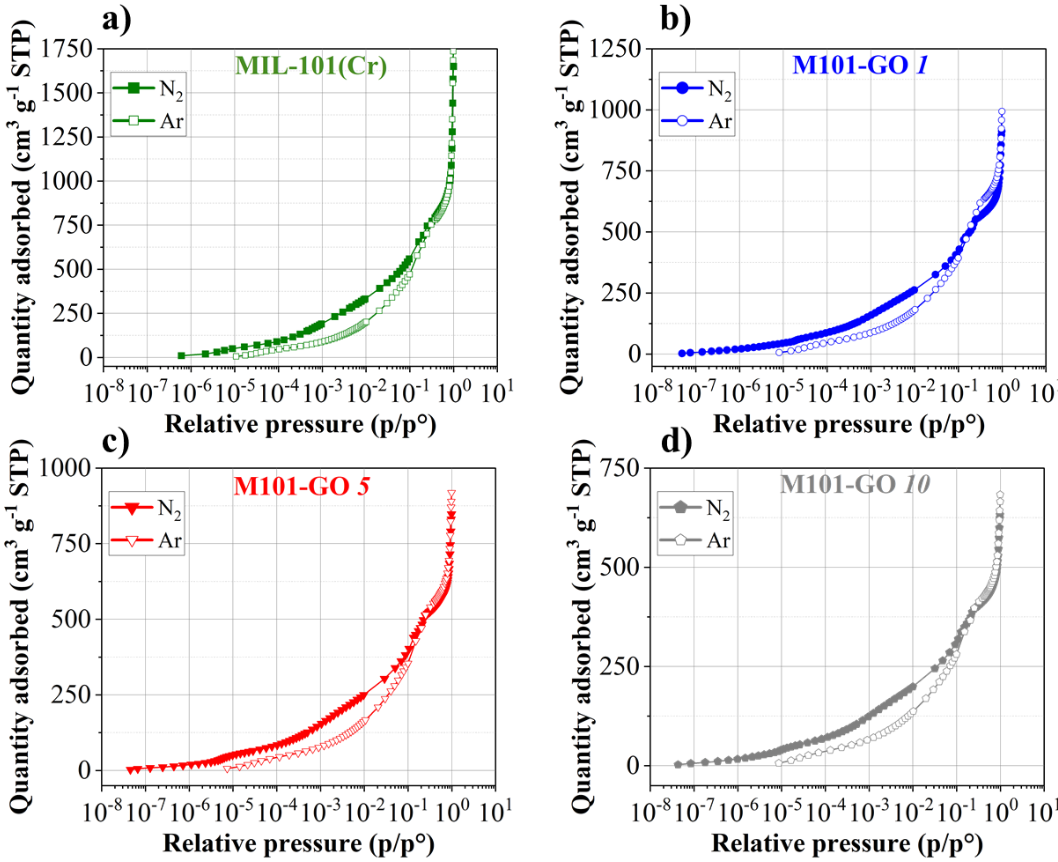

Figure S8: Comparison of nitrogen and argon adsorption isotherms (in semi-logarithmic scale) at 77 K and 87 K, respectively, for: a) MIL-101(Cr); b) M101-GO *1*; c) M101-GO *5*; and d) M101-GO *10*.

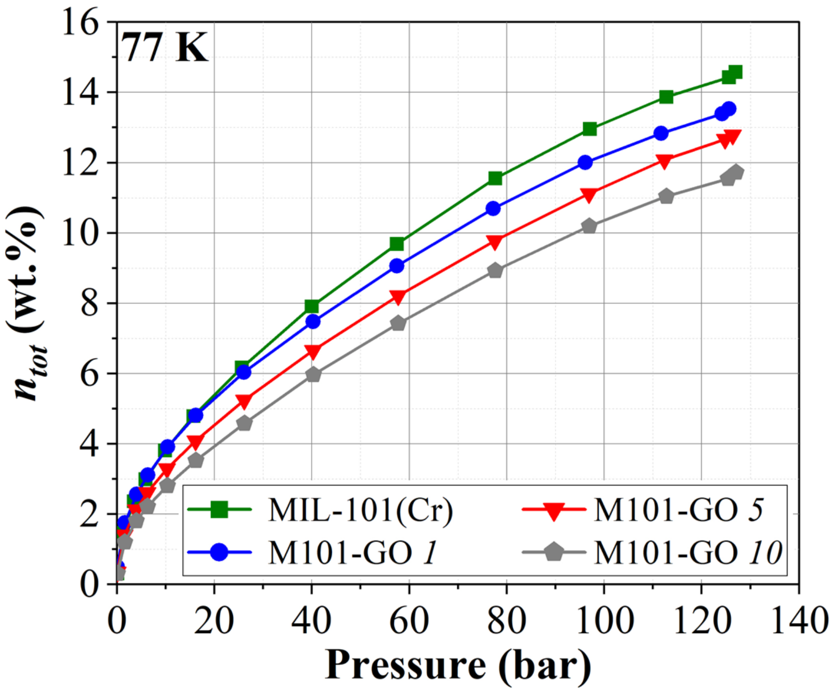

Figure S9: Total H_2 uptake at 77 K (n_{tot}, wt.%) of the MIL-101(Cr) and the hybrid materials.

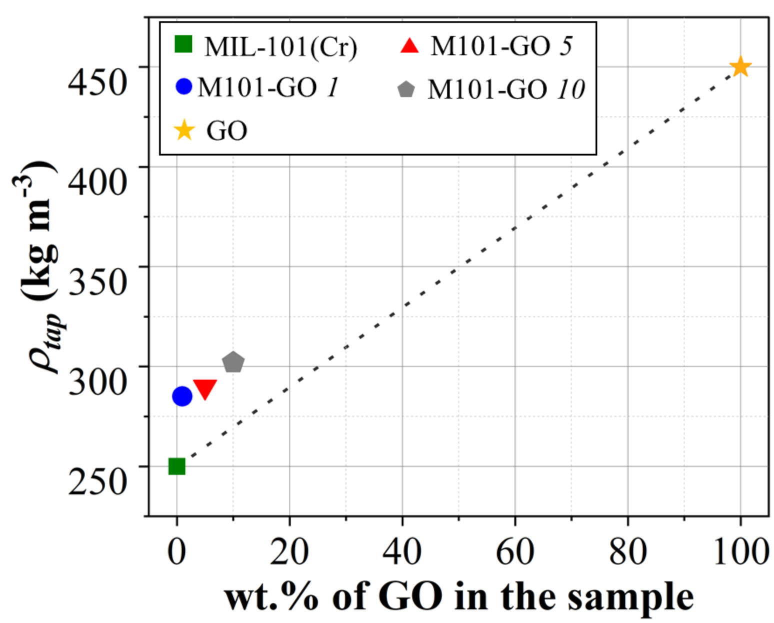

Figure S10: ρ_{tap} (kg m^{-3}) of all materials as a function of their wt.% GO.

Table S3: Total H_2 storage (kg m^{-3}) and release $^{77K\rightarrow160K,\ 77K\rightarrow77K}$ capacity of tanks either emplty or filled with MIL-101(Cr) and its hybrid materials.

Sample	*Total stored*	*Release $^{77K\rightarrow160K}$*		*Release $^{77K\rightarrow77K}$*	
	(kg m^{-3})	(kg m^{-3})	% Release	(kg m^{-3})	% Release
Empty tank	31	30.4	98	29.5	95
MIL-101(Cr)	33.83	32.50	96	26.74	79
M101-GO *1*	35.80	34.15	95	27.64	77
M101-GO *5*	33.63	32.35	96	26.67	79
M101-GO *10*	31.88	29.27	92	25.77	89

Table S4. Hydrogen storage capacities (n_{exc}) of selected MOFs reported in the literature under similar conditions (77 K, 20-60 bar).

Sample	Temperature (K)	Pressure (Bar)	A_{BET} (m^2 g^{-1})	Excess H_2 uptake (wt.%)	Ref.
HKUST-1	77	42	1116	2.80	[1]
HKUST-1@GO	77	42	734	3.60	[1]
MIL-101(Cr)	77	60	2887	2.90	[2]
MIL-101(Cr) @SWCNT	77	60	2998	4.40	[2]
MIL-101	77	100	3223	3.90	[3]
MIL101@AC	77	51	3542	4.40	[3]
IRMOF-2	77	25	1700	2.50	[4]
MFU-4l	77	20	1670	2.50	[5]
MIL-100(Al)	77	40	1200	3.10	[6]
MIL-100(Al)@Pd	77	40	380	1.30	[6]
MIL-101(Cr)	77	100	3542	6.00	[7]
MIL-101(Cr)	77	60	2887	2.90	[7]
MIL-101(Cr)@AC	77	60	2998	4.40	[7]
MOF-5	77	10-20	1758	1.20	[8]
MOF-5@CNT-Pt	77	10-20	1692	1.89	[8]
HKUST-1	77	10-20	1587	2.41	[9]
HKUST-1@Li	77	10-20	795	3.50	[9]
MIL-101(Cr)	77	10-20	2537	2.37	[9]
MIL-101(Cr)@Li	77	10-20	1840	3.39	[9]
HKUST-1	77	10-20	1456	2.49	[10]

HKUST-1@Pd	77	10-20	1033	3.68	[10]
MOF-5	77	10-20	921	1.46	[11]
MOF-5@Ni	77	10-20	802	1.53	[11]

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