

# Supporting Information

## **A step forward in understanding the hydrogen adsorption and compression on activated carbons**

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Table S1. Textural characteristics of the CACs.

Method	Parameter*	MSC30	MSP20X	SA1500	SA20	TH90I	Filtrisorb400
BET <sup>38</sup>	$A_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	3305	2363	2204	1737	1204	983
	$P/P_0$ range	0.05-0.2	0.04-0.1	0.05-0.018	0.05-0.2	0.02-0.07	0.01-0.08
NLDFT <sup>51,64</sup>	$S_{NLDFT}$ (m <sup>2</sup> g <sup>-1</sup> )	2216	2007	1621	1305	1256	996
	$V_T$ (cm <sup>3</sup> g <sup>-1</sup> )	1.596	0.935	1.331	1.190	0.495	0.469
	$V_{meso}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.641	0.053	0.670	0.698	0.028	0.095
	$V_{micro}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.955	0.882	0.661	0.492	0.467	0.374
	$V_{(<0.7nm)}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.056	0.211	0.055	0.056	0.216	0.149
	$V_{(0.7-2\text{ nm})}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.899	0.672	0.606	0.436	0.251	0.225
	$\bar{d}_T$ (nm)	1.949	1.212	3.211	3.795	1.448	3.036
	$\bar{d}_\mu$ (nm)	1.278	1.046	1.267	1.259	0.874	0.916
Dubinin – Radushkevich <sup>87</sup>	$V_{\mu, DR-N_2}$ (cm <sup>3</sup> g <sup>-1</sup> )	1.020	0.825	0.734	0.573	0.453	0.365
Dubinin – Radushkevich <sup>87</sup>	$V_{\mu, DR-CO_2}$ (cm <sup>3</sup> g <sup>-1</sup> )	0.379	0.450	0.307	0.237	0.299	0.241

\* $A_{BET}$ : surface area calculated by applying the BET equation to the nitrogen adsorption isotherms in the adequate  $P/P_0$  range . By integration of the PSDs obtained from the application of 2D-NLDFT-HS <sup>52</sup> model to N<sub>2</sub> and the CO<sub>2</sub> sorption data, we obtained the surface area,  $S_{NLDFT}$ ; total pore volumes,  $V_T$ , and the volumes of pores having diameters: (i) under 0.7 nm ( $V_{<0.7,NLDFT}$ ), *i.e.*, ultramicropores; (ii) between 0.7 and 2 nm ( $V_{0.7-2,NLDFT}$ ), *i.e.*, supermicropores; (iii) diameter under 2 nm ( $V_{micro}$ ), *i.e.*, micropores; and (iv) between 2 and 50 nm ( $V_{mes}$ ), *i.e.*, mesopores, calculated as  $V_T - V_{micro}$ . Micropore ( $\bar{d}_\mu$ ) and total ( $\bar{d}_T$ ) average pore sizes were calculated taking into account the PSDs and were volume-weighted. model  $V_T$ : total pore volume;  $V_{\mu, DR-N_2}$ : micropore volume calculated by applying the Dubinin – Radushkevich (DR) equation to the nitrogen adsorption isotherms;  $V_{\mu, DR-CO_2}$ : micropore volume (pores under 1 nm) determined by applying the Dubinin-Radushkevich (DR) equation to the carbon dioxide isotherms.

Table S2. MDA parameters of each CAC, obtained by application of Eq (1) to H<sub>2</sub> adsorption at eleven different temperatures, from 77 to 273 K (fits are shown in Fig. 6 for SA20 and SA1500).

CAC	$V_a$ (cm <sup>3</sup> g <sup>-1</sup> )	$n_{max}$ (mol kg <sup>-1</sup> )	$\alpha$ (J mol <sup>-1</sup> )	$\beta$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$P_0$ (MPa)
MSC30	1.504	72.5	3300	15.80	1013
SA20	0.723	36.7	3244	13.69	616
SA1500	0.868	46.2	3345	13.08	632
MSP20X	1.090	47.4	4094	11.50	632
TH90I	0.560	24.5	4699	9.72	655
Filtrisorb400	0.362	20.8	4300	9.75	700

Table S3. Determination coefficient when linearly fitting the MDA parameters, the isosteric heat or entropy of adsorption (at different fillings) to the textural parameters (the best fitting is in bold and on dark green and the worst one is on red).

		$V_{micro}$	$V_T$	$\bar{d}_\mu$	$S_{NLDFT}$	$A_{BET}$	$\bar{d}_T$
		(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(nm)	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	(nm)
Modified Dubinin-Astakhov parameters	$n_{max}$	0.85	0.8	0.55	0.88	<b>0.99</b>	0.04
	$\alpha$	0.17	0.84	<b>0.97</b>	0.19	0.43	0.31
	$\beta$	0.43	<b>0.95</b>	0.87	0.47	0.74	0.05
	$P_0$	0.32	0.25	0.1	0.33	<b>0.44</b>	0.06
	$V_a$	0.91	0.73	0.49	0.92	<b>0.98</b>	0.07
Isosteric heat of adsorption	$\Theta = 0.001$	0.17	0.87	<b>0.98</b>	0.2	0.43	0.25
	$\Theta = 0.0536$	0.17	0.87	<b>0.98</b>	0.2	0.43	0.25
	$\Theta = 0.2113$	0.17	0.87	<b>0.98</b>	0.2	0.43	0.25
	$\Theta = 0.5268$	0.17	0.87	<b>0.98</b>	0.2	0.43	0.25
	$\Theta = 0.9474$	0.17	0.87	<b>0.98</b>	0.2	0.43	0.25
Entropies of adsorption	$\Theta = 0.001$	<b>0.97</b>	0.65	0.39	<b>0.97</b>	<b>0.97</b>	<b>0.97</b>
	$\Theta = 0.0536$	0.91	0.73	0.47	0.92	<b>0.99</b>	0.91
	$\Theta = 0.2113$	0.89	0.75	0.49	0.91	<b>0.99</b>	0.89
	$\Theta = 0.5268$	0.87	0.76	0.5	0.89	<b>0.99</b>	0.87
	$\Theta = 0.9474$	0.86	0.77	0.51	0.88	<b>0.99</b>	0.86

Table S4. SIPS parameters obtained by fitting Eq. (5) to absolute hydrogen adsorption isotherms (fits are shown in Fig. S2 for SA20 and SA1500).

	Temperature (K)											
	77	93	113	133	153	173	193	213	233	253	273	
<b>MSC30</b>	<i>N</i>	45.59	35.02	30.13	25.72	23.79	18.51	17.55	13.95	13.29	12.51	10.30
	<i>b</i>	1.56	1.38	0.82	0.48	0.33	0.27	0.17	0.15	0.12	0.09	0.09
	<i>k</i>	0.63	0.72	0.81	0.87	0.92	0.98	0.98	1.05	0.96	0.98	1.01
<b>MSP20X</b>	<i>N</i>	33.42	32.68	27.00	24.75	23.42	18.46	17.43	15.07	12.99	12.19	10.05
	<i>b</i>	2.73	1.26	0.96	0.55	0.36	0.28	0.19	0.15	0.12	0.10	0.09
	<i>k</i>	0.64	0.61	0.72	0.78	0.84	0.89	0.93	0.95	0.97	0.98	1.01
<b>SA20</b>	<i>N</i>	21.26	19.34	18.24	16.50	13.50	12.76	10.63	10.38	9.39	8.79	7.18
	<i>b</i>	2.28	1.22	0.62	0.37	0.28	0.18	0.14	0.11	0.09	0.07	0.06
	<i>k</i>	0.72	0.73	0.77	0.83	0.89	0.92	0.95	0.92	1.04	1.00	1.03
<b>SA1500</b>	<i>N</i>	33.50	30.22	23.66	20.82	16.34	15.44	14.76	12.75	12.34	11.24	9.08
	<i>b</i>	1.26	0.83	0.64	0.39	0.29	0.19	0.14	0.11	0.08	0.07	0.06
	<i>k</i>	0.61	0.65	0.76	0.83	0.93	0.95	0.88	0.94	0.98	1.01	1.00
<b>TH90I</b>	<i>N</i>	18.75	18.65	15.52	13.45	11.23	10.94	8.86	8.61	8.55	8.25	5.53
	<i>b</i>	3.04	1.45	1.12	0.74	0.53	0.32	0.26	0.19	0.13	0.10	0.10
	<i>k</i>	0.60	0.50	0.63	0.72	0.81	0.83	0.92	0.93	0.95	0.94	1.00
<b>Filtrisorb400</b>	<i>N</i>	19.32	17.98	14.92	13.43	11.74	9.19	8.00	7.03	6.75	5.59	4.94
	<i>b</i>	1.52	1.01	0.83	0.54	0.38	0.32	0.25	0.18	0.14	0.11	0.10
	<i>k</i>	0.50	0.50	0.60	0.67	0.77	0.83	0.84	0.90	0.96	1.05	0.97

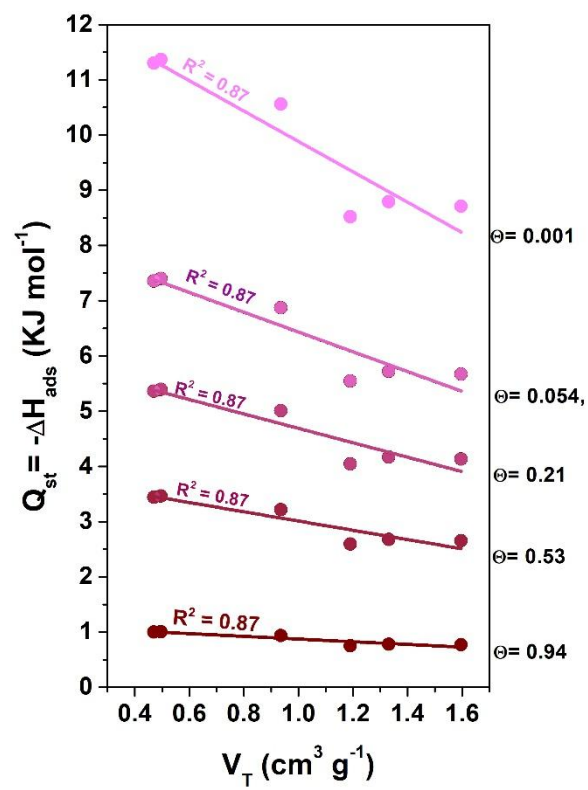


Figure S1. Evolution of  $Q_{st}$  as a function of total pore volume for several fractional fillings.

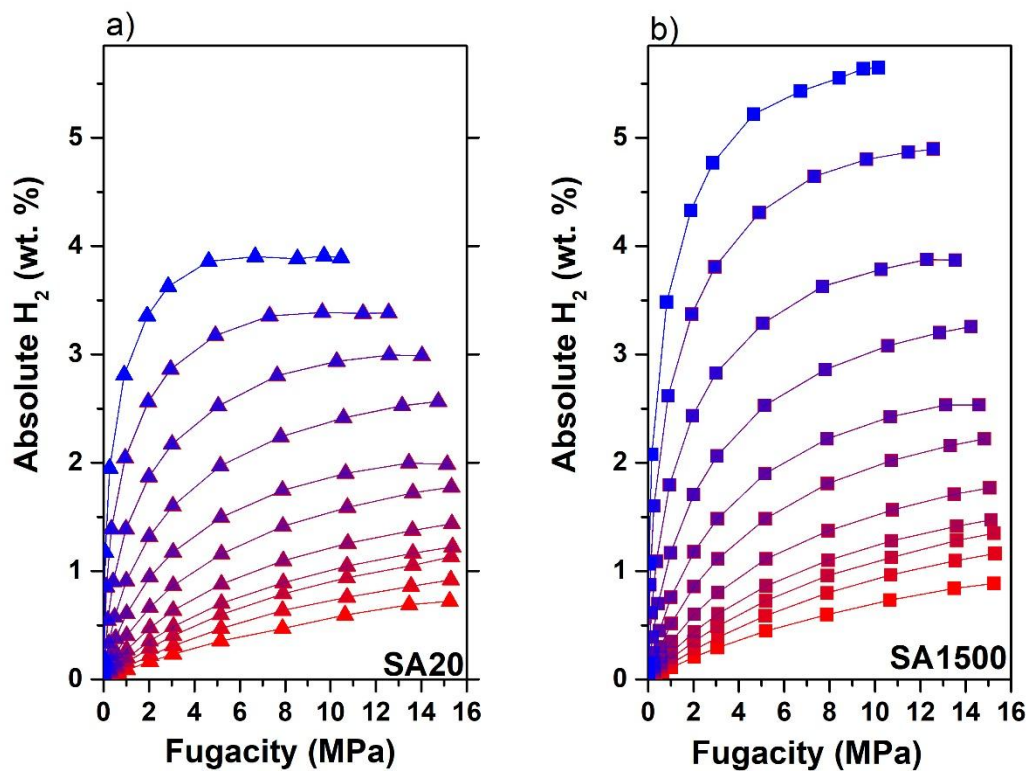


Figure S2. Absolute hydrogen adsorption isotherms of: (a) SA20; and (b) SA1500 fitted by the Sips equation.

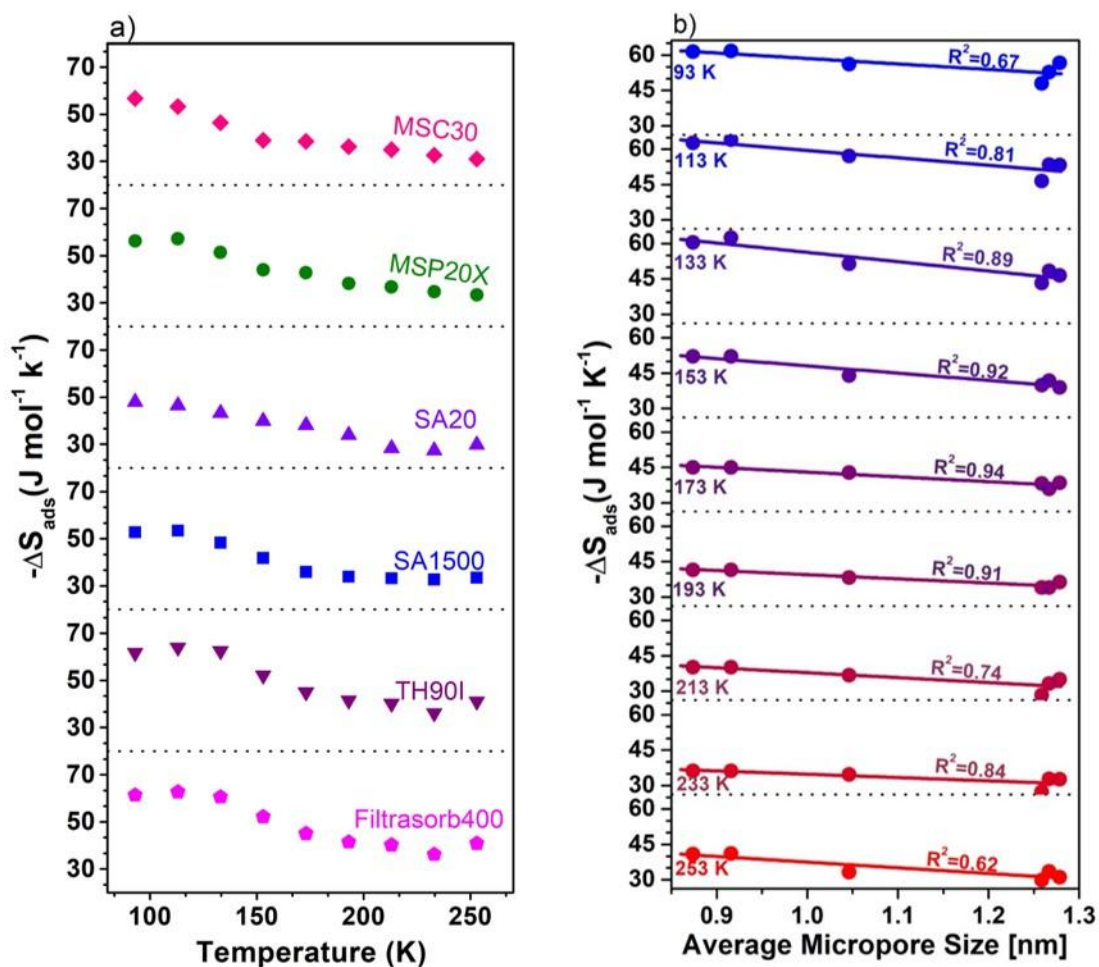


Figure S3. Average isosteric entropy of adsorption of the six CAC's as a function of the temperature at low amount adsorbed hydrogen (0-3.5 mmol $g^{-1}$ ) for: a) TH90I, b) Filtrasorb, c) MSP20, d) SA1500, e) SA20 and f) MSC30. Evolution of the average isosteric entropy of adsorption as a function of the average micropore size over the temperature range 93-253K: g) 93 and 113K, h) 133K, i) 153K j) 173K, k) 193 and 213K and l) 233 and 253K