# Supplementary Information to

**Is heteroatom doping of activated carbons always a good strategy for enhancing CO2 adsorption?**

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**SI 1**. Mathematical modeling of the equilibrium isotherms.

The Sips isotherm is a combination of Langmuir and Freundlich isotherms. Sips introduced a finite adsorption limit to Freundlich equation, and the mathematical form of the model is as follows:

|  |  |
| --- | --- |
|  | (SI1.1) |

where *qeq* is the equilibrium adsorbed amount (mol kg-1), *P* (bar) is the equilibrium pressure, *q*max (mol kg-1) is a constant reflecting the adsorption capacity at saturation, *b* (1/bar) is the Sips constant or affinity constant, and *n* (dimensionless) is the heterogeneity factor.

Isotherm parameters were obtained by non-linear fits of the aforementioned equations to the experimental CO2 equilibrium data using Origin software version 9.0, applying the Levenberg-Marquardt algorithm.

The isosteric heats of adsorption were obtained after fitting with the Sips model and using the Clausius-Clapeyron approach. To calculate equilibrium pressures as a function of the amount adsorbed using the Sips model fit, the pressure *P* in the Sips model equation is written in the following form:

|  |  |
| --- | --- |
|  | (SI1.2) |

The isosteric heats of adsorption were then plotted versus fractional coverage. The fractional coverage is represented by the following equation:

|  |  |
| --- | --- |
|  | (SI1.3) |

where *NA* (6.023×1023 molecules mol-1) is the Avogadro number, and *σ* (m2) is the cross-sectional area obtained from the Microactive software (σ = 1.14 × 10-19 m2 for CO2 and σ = 1.62 × 10-19 m2 for N2).

The selectivity of the materials to adsorb CO2 over N2 in a post-combustion scenario was estimated considering a binary mixture of CO2-N2 with volumetric fractions of and . The CO2/N2 selectivity was estimated with the following equation:

|  |  |
| --- | --- |
|  | (SI1.4) |

where and are the adsorbed amount of CO2 and N2 respectively in the binary mixture at a given pressure and temperature. The estimation of and was performed using the Ideal Adsorbed Solution Theory (IAST) with the Sips model.

The Ideal Adsorption Solution Theory (IAST), which was initially proposed by Myers and Prausnitz in 1965 [1], is a widely employed approach for predicting the equilibrium behavior of multi-component systems using data from single-component equilibria. This theory is founded on the premise that adsorbed molecules exhibit ideal solution behavior, signifying a lack of interactions among them, and it draws an analogy to Raoult's law:

|  |  |
| --- | --- |
|  | (SI1.6) |

where P is the total pressure, is the molar fraction of component *i* in the gas phase, is the hypothetical pressure of component *i* that results in the spreading pressure ( π ) of the mixture, is the molar fraction of the component *i* in the adsorbed phase. In order to determine the spreading pressure for a pure component, an expression derived from the Gibbs free energy is used as follows:

|  |  |
| --- | --- |
|  | (SI1.7) |

where is the adsorbed amount of component *i* from single isotherm data and *R* is the ideal gas constant. Under equilibrium, the surface potential of the mixture is equal to the surface potential of each single component. The spreading pressure must be the same for each component of the mixture () and can be expressed by an adsorption equilibrium equation (in this case the Sips model). The solution for that equation allows to find a relation between spreading pressure ( π ) and the standard pressure of each component ( ).

The total amount adsorbed in the mixture can be determined by the expression:

|  |  |
| --- | --- |
|  | (SI1.8) |

where is the total loading of the mixture. To determine the adsorbed amounts of each component in the gas mixture, a system of equations is necessary, which includes the single-component isotherm model as well as Equations (SI1.6), (SI1.7), and (SI1.8). Subsequently, upon reaching equilibrium, the adsorbed concentration can be calculated using the following expression:

|  |  |
| --- | --- |
|  | (SI1.9) |

References

[1] A.L. Myers, J.M. Prausnitz, Thermodynamics of Mixed-Gas Adsorption., AIChE J. 11 (1965) 121–127. https://doi.org/10.1002/aic.690110125.

**SI2.** Mathematical model used to simulate the breakthrough curves

The mass balance for each component of the fluid phase is given by Eq. (i):

(i)

where *Ci* is the gas phase concentration, *Dax* is the axial dispersion coefficient, *u* is the surface velocity, *yi* is the molar fraction, *kf,i* is the film mass transfer resistance, *Cpi* is the averaged concentration in the macropores, *Ct* is the total gas concentration, *εc* is the column void fraction, *ap* is the particle specific area, and *Bi* is the Biot number.

The mass balance in the macropores is described by Eq. (ii):

(ii)

where *Dp,i* is the macropore diffusivity, *rp* is the particle radius, *εp* is the particle void fraction, *ρp* is the particle density, and *qi* is the average adsorbed concentration.

The mass balance in the micropore is given by Eq. (iii):

(iii)

where *qeq,i* is the adsorbed concentration at equilibrium and *Dμ* is the coefficient diffusion in the micropores.

The Ergun equation is used to describe the behavior of the pressure drop along the column, as described by Eq. (iv):

 (iv)

where *P* is the total pressure, *μG* is the gas viscosity, *ρG* is the gas density and *dp* is the particle diameter.

The energy balance in the gas phase is given by Eq. (v):

(v)

where *T*, *Ts* and *TW* are the temperatures in the gas phase, adsorbent and column wall, respectively, *CPg* and *CVg* are the gas molar specific heats at constant pressure and volume, respectively, *rW* is the inner radius of the wall, *R* is ideal gas constant, *λ* is the axial heat dispersion coefficient, and *hW* and *hf* are the film heat transfer coefficients between the gas phase and wall, and between the gas phase and adsorbent, respectively.

The energy balance in the solid phase is described by Eq. (vi):

(vi)

where *CV,ads,i* is the molar specific heat at constant volume of the adsorbed phase, *CPs* is the mass heat capacity coefficient of the bed and is the bed density.

The energy balance of the column is given by Eq. (vii):

(vii)

where *CPw* is the specific heat of the wall, *U* is the overall heat transfer coefficient, *T∞* is the external temperature, *ρw* is the wall density, and *αw* and *αwl* are respectively the ratio of the internal surface area to the column wall volume, and the ratio of the logarithmic mean surface area of the column shell to the column wall volume.

The following table defines the most relevant parameters of the aforementioned partial equation system:

**Table 1.** Mathematical correlations used in the breakthrough modeling.

|  |  |
| --- | --- |
| ***Parameter*** | ***Mathematical correlation*** |
| *Macropore diffusion coefficient, Dp* |  |
| *Knudsen diffusivity, Dk* |  |
| *Molecular diffusivity, Dm* |  |
| *Film mass transfer resistance, kf* |  |
| *Heat transfer coefficient between the gas phase and wall, hw* |  |
| *Heat transfer coefficient between gas phase and adsorbent, hf* |  |
| *Axial heat dispersion coefficient, λ* |  |
| *Axial dispersion coefficient, Dax* |  |
| *Particle area to volume ratio,* |  |
| *Particle density,* |  |
| *Gas molar specific heat at constant volume,* |  |

where *Re* is the Reynolds number, *Sc* is the Schmidt number, *Pr* is the Prandtl number, *kg* is the gas thermal conductivity, *Dk* is the Knudsen diffusivity, *Dm* is the molecular diffusivity, is the particle tortuosity, and *MW* is the molecular weight of the gas.

Some parameters were considered constant with the following values:

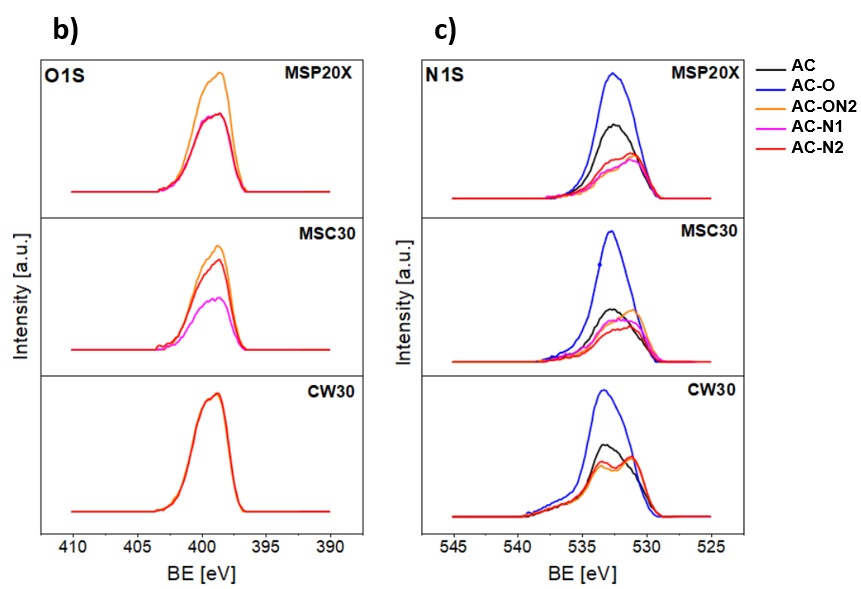
**Table 2.** Values of parameters used in the breakthrough modeling.

|  |  |
| --- | --- |
| ***Parameter*** | ***Value*** |
| *Tortuosity factor,* | *2* |
| *Overall heat transfer coefficient, U* | 1. *W m-2 K-1* |
| *Ambient temperature, T∞* | *303 K* |
| *Column void fraction, εc* | *0.37* |
| *Particle porosity, εp* | *0.46* |
| *Adsorbent calorific capacity at constant pressure, CPs* | *800 J kg-1 K-1* |

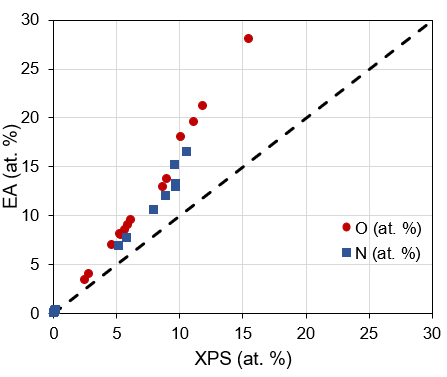
**SI3.** (a) Elemental analysis and XPS spectra of the three commercial ACs and their modified counterparts in the (b) O 1s and (c) N 1s regions.

**a)**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Carbon materials** | **C**  **(wt. %)** | **H**  **(wt. %)** | **O**  **(wt. %)** | **N**  **(wt. %)** | **C**  **(at. %)** | **H**  **(at. %)** | **O**  **(at. %)** | **N**  **(at. %)** |
| **MSP20X** | 95.5 | 0.25 | 3.37 | 0.11 | 97.1 | 1.53 | 1.29 | 0.05 |
| **MSP20X-O** | 86.8 | 1.25 | 12.9 | 0.04 | 87.5 | 7.56 | 4.88 | 0.02 |
| **MSP20X-N1** | 86.2 | 1.23 | 8.02 | 6.87 | 86.6 | 7.41 | 3.02 | 2.96 |
| **MSP20X-N2** | 85.8 | 1.07 | 6.95 | 10.5 | 86.4 | 6.46 | 2.62 | 4.53 |
| **MSP20X-ON2** | 80.4 | 1.45 | 9.50 | 13.2 | 81.8 | 8.85 | 3.62 | 5.75 |
| **MSC30** | 95.0 | 0.55 | 3.99 | 0.30 | 95.1 | 3.30 | 1.50 | 0.13 |
| **MSC30-O** | 87.6 | 1.33 | 13.7 | 0.16 | 86.9 | 7.92 | 5.10 | 0.07 |
| **MSC30-N1** | 82.8 | 1.42 | 8.51 | 7.68 | 84.7 | 8.71 | 3.26 | 3.37 |
| **MSC30-N2** | 79.0 | 1.63 | 8.09 | 12.0 | 81.5 | 10.1 | 3.13 | 5.30 |
| **MSC30-ON2** | 79.9 | 1.36 | 8.98 | 12.9 | 82.4 | 8.42 | 3.47 | 5.70 |
| **CW30** | 77.5 | 3.21 | 19.5 | 0.22 | 74.4 | 18.5 | 7.02 | 0.09 |
| **CW30-O** | 73.9 | 3.33 | 28.0 | 0.22 | 70.7 | 19.1 | 10.1 | 0.09 |
| **CW30-N2** | 69.2 | 2.99 | 21.2 | 15.1 | 68.1 | 17.7 | 7.83 | 6.37 |
| **CW30-ON2** | 68.0 | 3.17 | 18.0 | 16.5 | 67.4 | 18.9 | 6.69 | 7.01 |
|  |  |  |  |  |  |  |  |  |



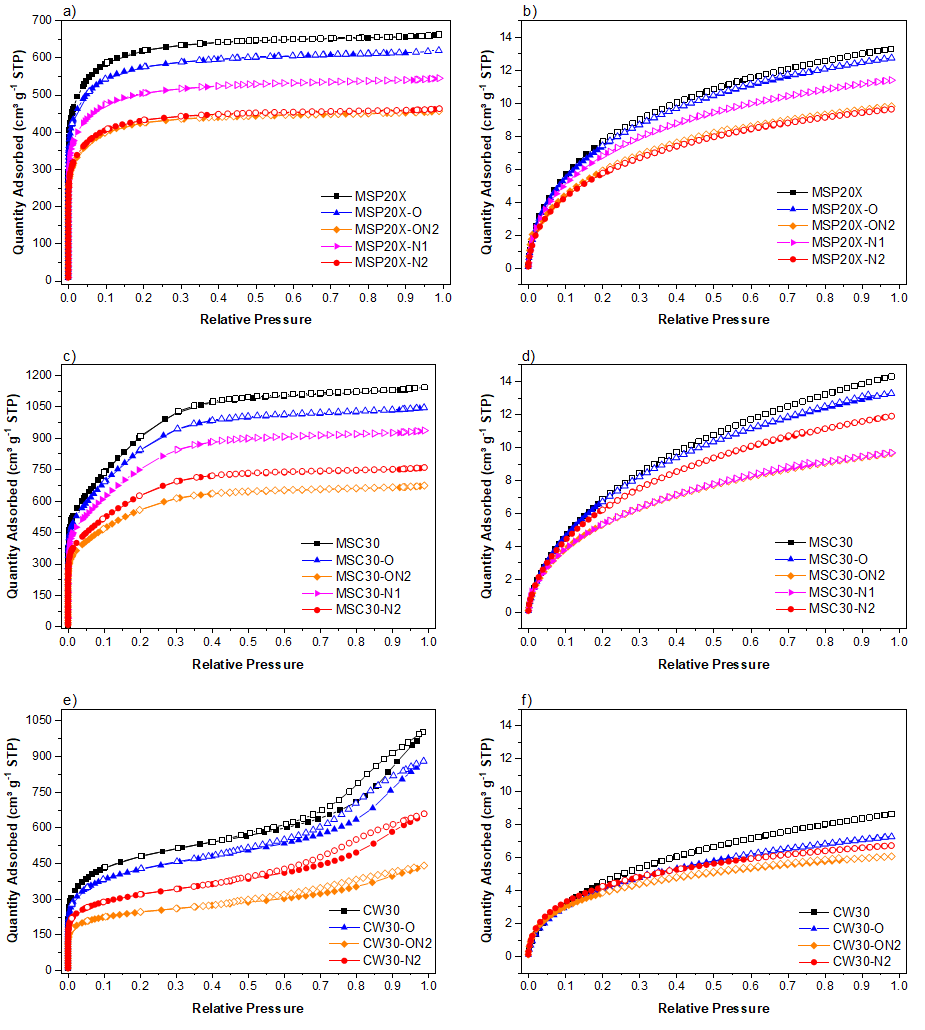
**d)**



**SI 4.** Surface composition by XPS.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Carbon materials** | **Carbon (C) [at. %]** | | | | | | **Oxygen (O) [at. %]** | | | | | **Nitrogen (N) [at. %]** | | | | | |
| **C I** | **C II** | **C III** | **C IV** | **C V** | **total** | **O I** | **O II** | **O III** | **O IV** | **total** | **N6** | **N5** | **N-Q** | **N-X** | **total** |
| **MSP20X** | 59.7 | 24.7 | 5.9 | 3.4 | 0.9 | **94.7** | 1.5 | 3.6 | 0.1 | 0.0 | **5.2** | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| **MSP20X-O** | 55.4 | 23.9 | 4.8 | 4.8 | 1.8 | **90.8** | 2.1 | 5.1 | 0.0 | 0.0 | **7.2** | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| **MSP 20X-ON2** | 50.0 | 24.4 | 9.7 | 2.5 | 2.1 | **88.7** | 1.6 | 0.8 | 0.2 | 0.0 | **2.5** | 3.3 | 4.6 | 0.8 | 0.0 | **8.7** |
| **MSP 20X-N1** | 53.3 | 26.1 | 7.7 | 2.4 | 1.5 | **90.9** | 1.4 | 1.2 | 0.1 | 0.1 | **2.7** | 2.2 | 3.6 | 0.7 | 0.0 | **6.4** |
| **MSP 20X-N2** | 52.3 | 26.3 | 8.2 | 2.0 | 1.9 | **90.7** | 1.6 | 1.4 | 0.2 | 0.0 | **3.1** | 2.1 | 3.2 | 0.8 | 0.0 | **6.1** |
| **MSC30** | 57.3 | 27.6 | 6.5 | 3.9 | 2.0 | **97.3** | 0.7 | 1.8 | 0.2 | 0.1 | **2.8** | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| **MSC30-O** | 54.5 | 25.5 | 8.2 | 4.4 | 2.3 | **94.9** | 0.9 | 4.3 | 0.4 | 0.1 | **5.7** | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| **MSC30-ON2** | 49.7 | 25.3 | 10.1 | 0.9 | 3.2 | **89.1** | 1.5 | 1.0 | 0.1 | 0.1 | **2.6** | 3.5 | 3.9 | 0.9 | 0.0 | **8.3** |
| **MSC30-N1** | 54.1 | 26.2 | 8.6 | 2.1 | 2.1 | **93.1** | 1.0 | 1.3 | 0.1 | 0.1 | **2.5** | 1.5 | 2.3 | 0.5 | 0.0 | **4.4** |
| **MSC30-N2** | 50.8 | 24.0 | 10.1 | 1.0 | 2.9 | **88.8** | 1.1 | 1.0 | 0.1 | 0.1 | **2.3** | 3.6 | 4.1 | 1.2 | 0.0 | **8.9** |
| **CW30** | 65.8 | 19.4 | 5.9 | 1.1 | 1.5 | **93.8** | 1.7 | 3.8 | 0.1 | 0.5 | **6.1** | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| **CW30-O** | 63.1 | 16.9 | 6.6 | 1.6 | 0.8 | **89.0** | 2.9 | 7.4 | 0.1 | 0.6 | **11.0** | 0.0 | 0.0 | 0.0 | 0.0 | **0.0** |
| **CW30-ON2** | 45.9 | 26.6 | 8.8 | 0.7 | 0.6 | **82.5** | 2.8 | 2.1 | 0.6 | 0.5 | **6.0** | 4.3 | 6.2 | 1.0 | 0.0 | **11.4** |
| **CW30-N2** | 47.0 | 25.9 | 8.9 | 0.8 | 0.6 | **83.2** | 2.8 | 2.1 | 0.7 | 0.5 | **6.0** | 4.1 | 6.3 | 0.3 | 0.0 | **10.8** |

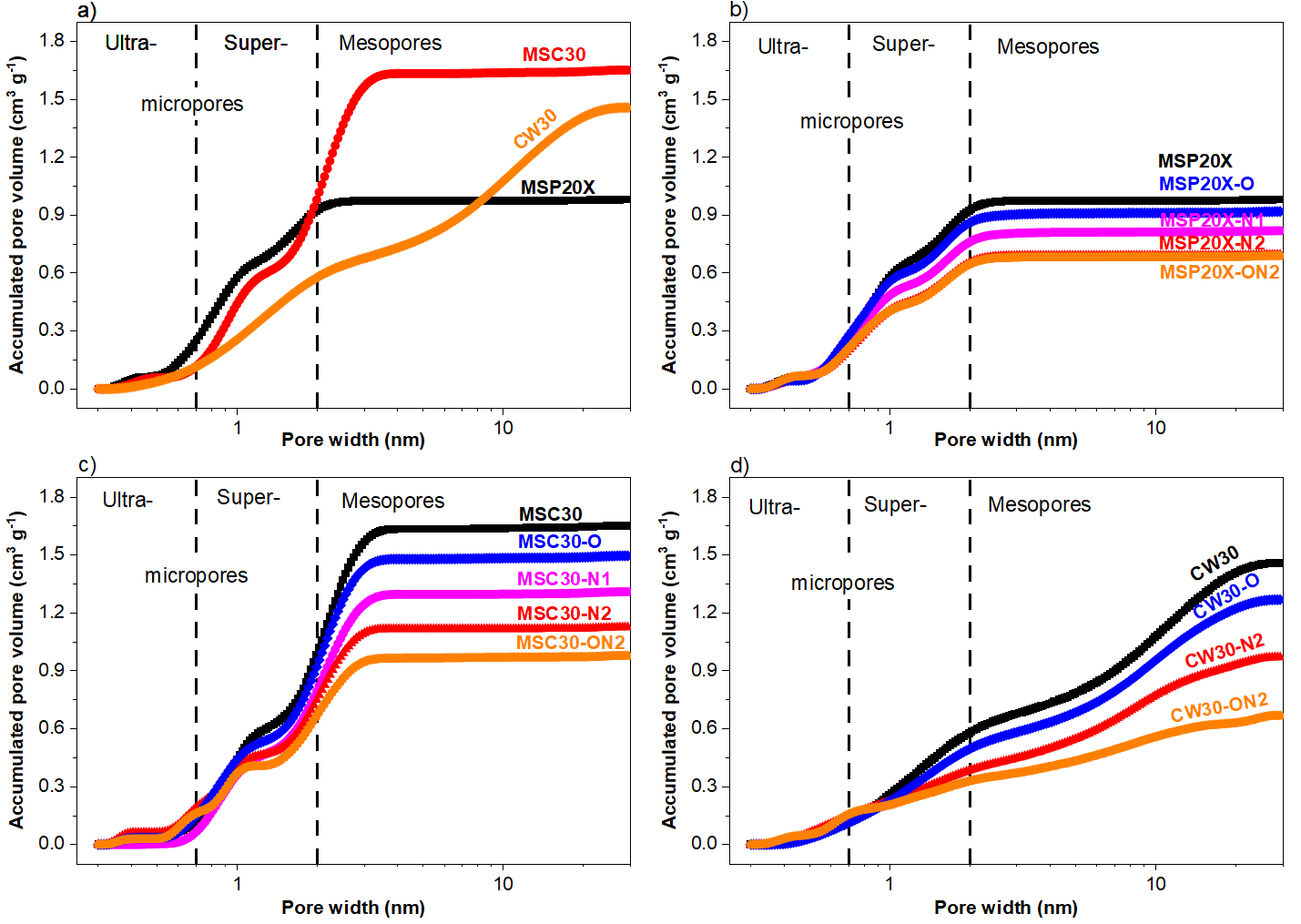
**SI 5.** N2 (a, c, e) and H2 (b, d, f) adsorption-desorption isotherms for: (a) and (b) MSP20X series; (c) and (d) MSC30 series; and (e) and (f) CW30 series. Solid symbols represent the adsorption branch, while empty symbols represent the desorption branch.



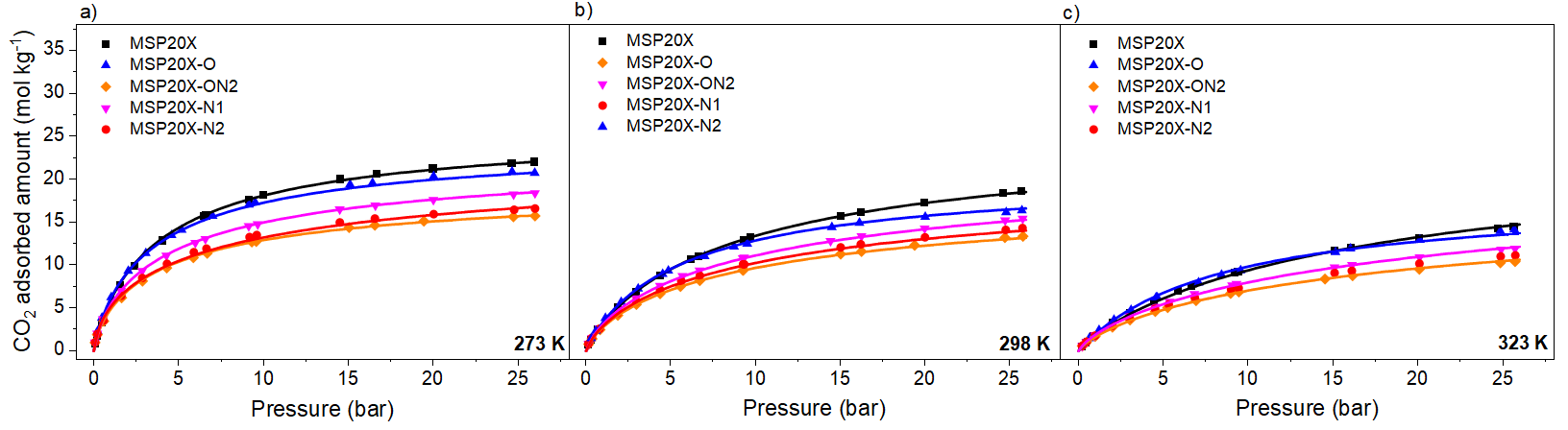
**SI 6**. Textural properties calculated from N2 and H2 adsorption isotherms.

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Carbon**  **material** | **Textural Properties** | | | | | | | | | | | | | |
| **ABET**  [m2/g] | **SNLDFT**  [m2/g] | **Vµ-DR N2**  [cm3/g] | **VT**  [cm3/g] | **VMES**  [cm3/g] | **V ult-µicro**  [cm3/g] | **V sup-µicro**  [cm3/g] | **V µicro**  [cm3/g] | **L0 ult-µicro**  [nm] | **L0 sup-µicro**  [nm] | **L0 µicro**  [nm] | **L0 meso**  [nm] | **L0**  [nm] |
| **MSP20X** | 3200 | 2284 | 0.87 | 0.98 | 0.05 | 0.25 | 0.68 | 0.93 | 0.56 | 1.16 | 1.00 | 3.95 | 1.16 |
| **MSP20X-N1** | 2661 | 1948 | 0.69 | 0.82 | 0.06 | 0.24 | 0.52 | 0.76 | 0.56 | 1.18 | 0.98 | 4.50 | 1.22 |
| **MSP20X-N2** | 2230 | 1650 | 0.58 | 0.70 | 0.04 | 0.20 | 0.45 | 0.65 | 0.56 | 1.19 | 0.99 | 4.31 | 1.19 |
| **MSP20X-O** | 2982 | 2170 | 0.78 | 0.92 | 0.06 | 0.28 | 0.58 | 0.86 | 0.57 | 1.17 | 0.98 | 5.02 | 1.22 |
| **MSP20X-ON2** | 1981 | 1668 | 0.57 | 0.69 | 0.04 | 0.21 | 0.44 | 0.65 | 0.55 | 1.20 | 0.99 | 4.86 | 1.22 |
| **MSC30** | 2344 | 2522 | 1.18 | 1.65 | 0.66 | 0.12 | 0.88 | 1.00 | 0.54 | 1.29 | 1.20 | 2.89 | 1.87 |
| **MSCC30-N1** | 1901 | 1918 | 0.90 | 1.31 | 0.50 | 0.07 | 0.74 | 0.80 | 0.64 | 1.28 | 1.23 | 2.90 | 1.87 |
| **MSCC30-N2** | 1630 | 2029 | 0.77 | 1.13 | 0.37 | 0.19 | 0.57 | 0.76 | 0.54 | 1.33 | 1.13 | 2.88 | 1.70 |
| **MSC30-O** | 2178 | 2357 | 1.02 | 1.50 | 0.56 | 0.15 | 0.79 | 0.93 | 0.58 | 1.31 | 1.20 | 2.90 | 1.83 |
| **MSC30-ON2** | 1600 | 1722 | 0.67 | 0.98 | 0.30 | 0.16 | 0.51 | 0.67 | 0.56 | 1.32 | 1.14 | 3.10 | 1.75 |
| **CW30** | 1736 | 1521 | 0.63 | 1.46 | 0.88 | 0.12 | 0.46 | 0.58 | 0.55 | 1.24 | 1.11 | 9.77 | 6.32 |
| **CW30-N2** | 1157 | 1192 | 0.42 | 0.97 | 0.59 | 0.15 | 0.24 | 0.38 | 0.53 | 1.24 | 0.97 | 9.04 | 5.84 |
| **CW30-O** | 1540 | 1325 | 0.54 | 1.27 | 0.77 | 0.11 | 0.38 | 0.50 | 0.56 | 1.26 | 1.10 | 9.57 | 6.25 |
| **CW30-ON2** | 898 | 1032 | 0.32 | 0.67 | 0.34 | 0.16 | 0.17 | 0.33 | 0.54 | 1.26 | 0.92 | 9.17 | 5.10 |

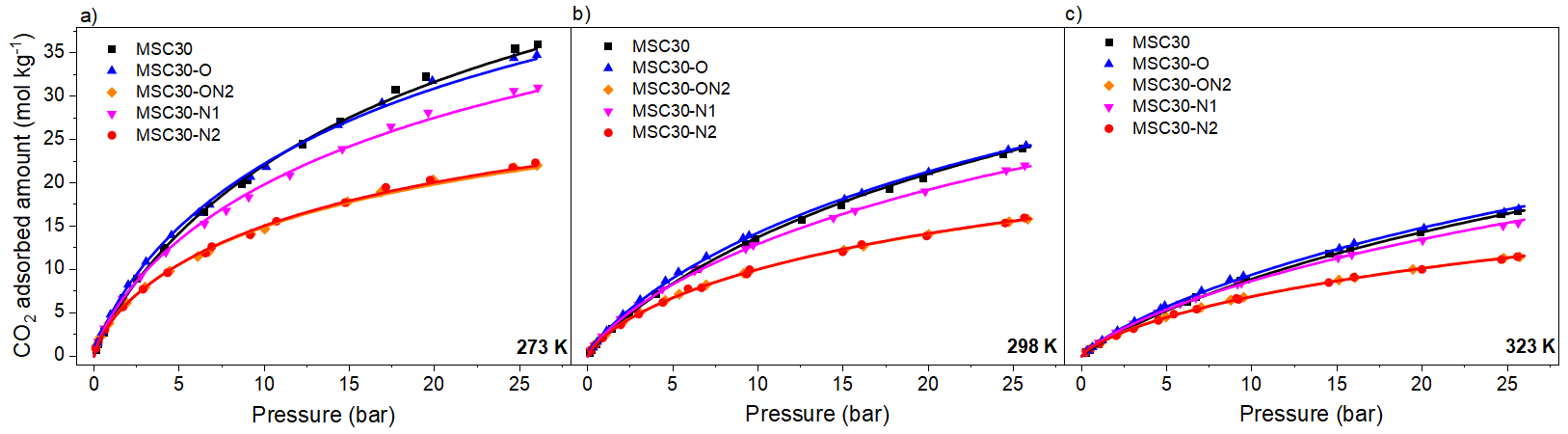
**SI 7.** Cumulative pore volumes calculated by the 2D-NLDFT model for: (a) raw, commercial ACs; (b) MSP20X series; (c) MSC30 series; and (d) CW30 series.

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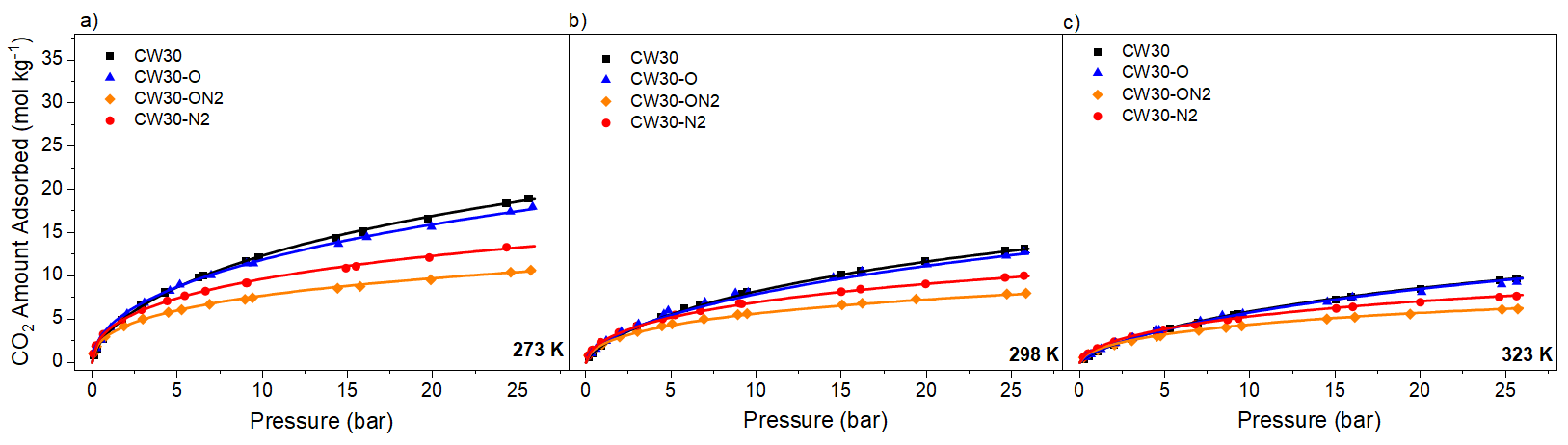
**SI 8.** CO2 adsorption isotherms at: (a) 273; (b) 298; and (c) 323 K, and up to 25 bar for the MSP20X series. Solid lines represent the fits of the Sips adsorption model.



**SI 9.** CO2 adsorption isotherms at: (a) 273; (b) 298; and (c) 323 K, and up to 25 bar for the MSC30X series. Solid lines represent the fits of the Sips adsorption model.



**SI 10.** CO2 adsorption isotherms at: (a) 273; (b) 298; and (c) 323 K, and up to 25 bar for the CW30 series. Solid lines represent the fits of the Sips adsorption model.



**SI 11.** Parameters obtained by application of the Sips model to the a) CO2 adsorption isotherms for all samples and b) N2 adsorption isotherms for the MSP20X series.

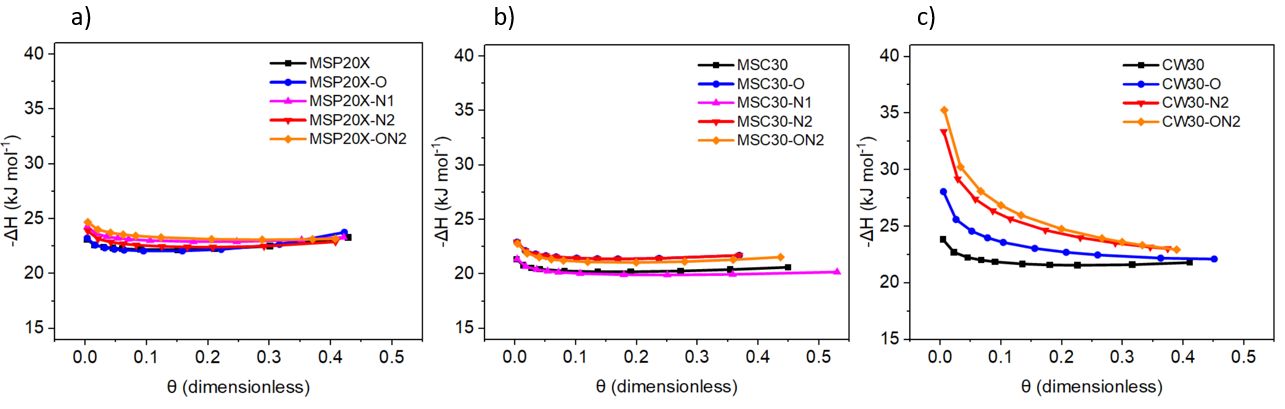
**a)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Material | Temperature [K] | *qmax* [mol/kg] | b [bar] | n | R2 |
| **MSP20X** | 273 | 26.1 | 0.242 | 0.88 | 1.00 |
| 298 | 24.9 | 0.116 | 0.89 | 1.00 |
| 323 | 23.8 | 0.062 | 0.89 | 1.00 |
| **MSP20X-O** | 273 | 24.1 | 0.266 | 0.85 | 1.00 |
| 298 | 21.3 | 0.152 | 0.88 | 1.00 |
| 323 | 18.8 | 0.095 | 0.91 | 0.99 |
| **MSP20X-ON2** | 273 | 19.1 | 0.214 | 0.75 | 1.00 |
| 298 | 18.8 | 0.096 | 0.76 | 1.00 |
| 323 | 18.4 | 0.048 | 0.77 | 1.00 |
| **MSP20X-N1** | 273 | 23.1 | 0.214 | 0.78 | 1.00 |
| 298 | 22.4 | 0.099 | 0.78 | 1.00 |
| 323 | 21.7 | 0.051 | 0.79 | 1.00 |
| **MSP20X-N2** | 273 | 18.6 | 0.216 | 0.76 | 1.00 |
| 298 | 18.4 | 0.097 | 0.77 | 1.00 |
| 323 | 18.3 | 0.049 | 0.78 | 1.00 |
| **MSC30** | 273 | 78.8 | 0.032 | 0.81 | 1.00 |
| 298 | 70.5 | 0.018 | 0.82 | 1.00 |
| 323 | 63.1 | 0.011 | 0.83 | 1.00 |
| **MSC30-O** | 273 | 69.3 | 0.036 | 0.78 | 1.00 |
| 298 | 62.4 | 0.021 | 0.79 | 1.00 |
| 323 | 56.2 | 0.013 | 0.80 | 1.00 |
| **MSC30-ON2** | 273 | 43.2 | 0.037 | 0.70 | 1.00 |
| 298 | 38.9 | 0.021 | 0.71 | 1.00 |
| 323 | 35.1 | 0.013 | 0.72 | 1.00 |
| **MSC30-N1** | 273 | 67.1 | 0.029 | 0.75 | 1.00 |
| 298 | 61.3 | 0.017 | 0.76 | 1.00 |
| 323 | 56.1 | 0.010 | 0.76 | 1.00 |
| **MSC30-N2** | 273 | 44.3 | 0.035 | 0.70 | 1.00 |
| 298 | 40.7 | 0.019 | 0.70 | 1.00 |
| 323 | 37.4 | 0.011 | 0.71 | 1.00 |
| **CW30** | 273 | 35.6 | 0.037 | 0.69 | 1.00 |
| 298 | 32.5 | 0.021 | 0.70 | 1.00 |
| 323 | 29.7 | 0.013 | 0.71 | 1.00 |
| **CW30-O** | 273 | 36.7 | 0.027 | 0.62 | 1.00 |
| 298 | 33.6 | 0.016 | 0.64 | 0.99 |
| 323 | 30.7 | 0.010 | 0.66 | 0.99 |
| **CW30-ON2** | 273 | 22.1 | 0.023 | 0.48 | 1.00 |
| 298 | 20.8 | 0.013 | 0.51 | 1.00 |
| 323 | 19.5 | 0.008 | 0.54 | 1.00 |
| **CW30-N2** | 273 | 27.1 | 0.019 | 0.50 | 1.00 |
| 298 | 25.2 | 0.011 | 0.52 | 1.00 |
| 323 | 23.5 | 0.007 | 0.55 | 1.00 |

**b)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Material | Temperature [K] | *qmax* [mol/kg] | b [bar] | n | R2 |
| **MSP20X** | 273 | 11.1 | 0.068 | 0.93 | 1.00 |
| 298 | 11.0 | 0.039 | 0.94 | 1.00 |
| 323 | 10.9 | 0.024 | 0.95 | 1.00 |
| **MSP20X-O** | 273 | 10.9 | 0.062 | 0.93 | 1.00 |
| 298 | 10.8 | 0.035 | 0.94 | 1.00 |
| 323 | 10.7 | 0.022 | 0.95 | 1.00 |
| **MSP20X-ON2** | 273 | 9.49 | 0.061 | 0.91 | 1.00 |
| 298 | 9.40 | 0.035 | 0.92 | 1.00 |
| 323 | 9.32 | 0.022 | 0.92 | 1.00 |
| **MSP20X-N1** | 273 | 7.36 | 0.078 | 0.97 | 1.00 |
| 298 | 7.29 | 0.045 | 0.98 | 1.00 |
| 323 | 7.23 | 0.028 | 0.99 | 1.00 |
| **MSP20X-N2** | 273 | 7.76 | 0.064 | 0.92 | 1.00 |
| 298 | 7.68 | 0.037 | 0.93 | 1.00 |
| 323 | 7.61 | 0.023 | 0.94 | 1.00 |

**SI 12.** Isosteric heat of adsorption calculated using the Clausius-Clapeyron equation on data from fitted isotherms (Sips model) as a function of CO2 fractional coverage: (a) MSP20X, (b) MSC30, and (c) CW30 series.



**SI 13.** Average isosteric heats of adsorption of a) CO2 (coverage up to 0.5) of commercial and chemically modified ACs and b) N2 (coverage up to 0.2) of MSP20X series.

**a)**

| **Carbon material** | ***-ΔHisost***  **[kJ/mol]** |
| --- | --- |
| **MSP20X** | 22.5 |
| **MSP20X-O** | 22.6 |
| **MSP20X-N1** | 23.3 |
| **MSP20X-N2** | 22.8 |
| **MSP20X-ON2** | 23.5 |
| **MSC30** | 20.5 |
| **MSC30-O** | 21.8 |
| **MSC30-N1** | 20.3 |
| **MSC30-N2** | 21.8 |
| **MSC30-ON2** | 21.5 |
| **CW30** | 20.5 |
| **CW30-O** | 23.8 |
| **CW30-N2** | 26.0 |
| **CW30-ON2** | 26.5 |

**b)**

| **Carbon material** | ***-ΔHisost***  **[kJ/mol]** |
| --- | --- |
| **MSP20X** | 15.98 |
| **MSP20X-O** | 15.98 |
| **MSP20X-N1** | 16.02 |
| **MSP20X-N2** | 15.87 |
| **MSP20X-ON2** | 15.95 |

**SI 14.** Pore volume distribution according to Equation (2).

|  |  |
| --- | --- |
|  | (Eq. 2) |

|  |  |  |  |
| --- | --- | --- | --- |
| **Pore volumes** | | | |
| **Carbon material** | V w<0.7 | V0.7 <w <2 | V2<w<50 |
| [cm3/g] | [cm3/g] | [cm3/g] |
| **MSP20X** | 0.246 | 0.676 | 0.055 |
| **MSP20X-N1** | 0.241 | 0.519 | 0.057 |
| **MSP20X-N2** | 0.201 | 0.452 | 0.041 |
| **MSP20X-O** | 0.275 | 0.584 | 0.056 |
| **MSP20X-ON2** | 0.209 | 0.436 | 0.042 |
| **MSC30** | 0.116 | 0.878 | 0.657 |
| **MSC30-N1** | 0.067 | 0.737 | 0.505 |
| **MSC30-N2** | 0.185 | 0.566 | 0.367 |
| **MSC30-O** | 0.146 | 0.786 | 0.562 |
| **MSC30-ON2** | 0.16 | 0.511 | 0.305 |
| **CW30** | 0.116 | 0.463 | 0.878 |
| **CW30-N2** | 0.148 | 0.237 | 0.586 |
| **CW30-O** | 0.113 | 0.384 | 0.772 |
| **CW30-ON2** | 0.155 | 0.173 | 0.339 |

**S15.** Parameters *a, b, c,* and *d* of Equation (2) at different pressures and temperatures.

|  |  |  |  |
| --- | --- | --- | --- |
| |  |  | | --- | --- | |  | (Eq. 2) | |  |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **273K** | | | | |
| Pressure | ***a*** | ***b*** | ***c*** | ***d*** |
| [bar] | [mmol/cm3] | [mmol/cm3] | [mmol/cm3] | [mmol/g at.%] |
| **0.25** | 5.37 | 0.763 | 0.0466 | 0.0566 |
| **0.5** | 8.38 | 1.7 | 0.143 | 0.0536 |
| **1** | 11.8 | 3.42 | 0.22 | 0.0557 |
| **2** | 15.6 | 6.84 | 0.22 | 0.0512 |
| **5** | 15.6 | 14.4 | 0.22 | 0.0684 |
| **7** | 17.3 | 17.3 | 0.89 | 0.0459 |
| **10** | 20.2 | 20.2 | 2.35 | 0 |
| **15** | 23.3 | 23.3 | 4.55 | 0 |
| **25** | 26.1 | 26.1 | 9.19 | 0 |
| **298K** | | | | |
| Pressure | ***a*** | ***b*** | ***c*** | ***d*** |
| [bar] | [mmol/cm3] | [mmol/cm3] | [mmol/cm3] | [mmol/g at.%] |
| **0.25** | 2.58 | 0.381 | 2.23E-07 | 0.0356 |
| **0.5** | 4.22 | 0.874 | 4.62E-07 | 0.0455 |
| **1** | 6.59 | 1.82 | 1.23E-05 | 0.0556 |
| **2** | 9.87 | 3.67 | 5.00E-05 | 0.0591 |
| **5** | 12.9 | 8.45 | 5.00E-05 | 0.0661 |
| **7** | 13 | 11.1 | 6.68E-05 | 0.0745 |
| **10** | 14.1 | 14.1 | 6.68E-05 | 0.0715 |
| **15** | 17.1 | 17.1 | 1.37 | 0.0295 |
| **25** | 21.9 | 21.9 | 1.37 | 0 |
| **323K** | | | | |
| Pressure | ***a*** | ***b*** | ***c*** | ***d*** |
| [bar] | [mmol/cm3] | [mmol/cm3] | [mmol/cm3] | [mmol/g at.%] |
| **0.25** | 1.4 | 0.203 | 2.23E-07 | 0.0213 |
| **0.5** | 2.45 | 0.456 | 4.62E-07 | 0.03 |
| **1** | 4.08 | 1.01 | 1.23E-05 | 0.0381 |
| **2** | 6.4 | 2.1 | 1.23E-05 | 0.0461 |
| **5** | 10.1 | 5.08 | 1.23E-05 | 0.0517 |
| **7** | 11.2 | 6.87 | 6.68E-05 | 0.0547 |
| **10** | 11.6 | 9.21 | 6.68E-05 | 0.0607 |
| **15** | 12.4 | 12.4 | 0.000178 | 0.0654 |
| **25** | 15.9 | 15.9 | 1.37 | 0.0177 |