

Microporous volumes from nitrogen adsorption at 77 K: when to use a different standard isotherm?

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Supporting Information

S1 Method for the preparation of the char and the activated carbons

A mixture of industrial crude glycerin (82% glycerol, from a Portuguese company) and sulfuric acid (95-97%, Sigma-Aldrich) was prepared using a volume ratio (1:0.5). The flask was stirred at room temperature until foaming ceased, typically for ~30 minutes adapting the procedure described elsewhere [1]. Then, the mixture was transferred to an autoclave (Teflon-lined, stainless-steel) and the acid carbonization was made at 180 °C for 6 h in an oven (Medline Sci. Ltd., mod. ON-02G). The acid glycerin-*char* was washed (distilled water until pH 7) and dried at 100 °C. The obtained solid was crushed to a fine powder (dimensions < 0.297 mm). The glycerin-*char* (1 g) was mixed with the adequate KOH amount dissolved ~ 10 cm³ of distilled water, followed by stirring for 2 h at ambient temperature, and then dried at 100 °C until complete water evaporation. The samples were activated at 700 °C and KOH:char weight ratios were 1:1 (for the material C2) and 2:1 for the material C1. The mixture was activated in a horizontal furnace (Thermolyne, model 21100) under N₂ flow (5 cm³ s⁻¹). The temperature was raised (10 °C min⁻¹) up to the activation temperature and kept for 1 h. After the chemical activation process, post-chemical activation was required to remove excess activating agent from the activated carbons. The glycerin-*activated carbons* were treated with HCl solution (1M), then washed with distilled water until pH 7, and dried at 100 °C to allow the evaporation of the excess water. The sample C3 was a commercial sample from Norit.

S2. Mathematical expressions for the various standard isotherms

For the universal *t*-curve the expression from Lippens and de Boer [2] was used:

$$t/\text{\AA} = \left[\frac{13.99}{0.034 - \log(p/p^0)} \right]^{0.5}$$

For the hydroxylated silica [3], the carbon [4] and the char, all used in the form of α_s -

plots, a polynomial equation of the type $\alpha_s = A_0 + A_1 (p/p^0) + A_2 (p/p^0)^2 + A_3$

$(p/p^0)^3$...was employed and the coefficients A0 to A9 are given in Table S1.

Table S1 Coefficients of the polynomial equations that relate α_s and the relative pressure (p/p^0) for the standard isotherms on the hydroxylated silica, the carbon and the char

| | carbon | hydroxylated silica | char |
|----|------------|---------------------|---------|
| A0 | 0.4964302 | 0.27692439 | 0.9646 |
| A1 | 4.2880233 | 13.403724 | -7.4791 |
| A2 | -47.262408 | -204.06097 | 74.791 |
| A3 | 338.6696 | 1728.6363 | -291.64 |
| A4 | -1432.0171 | -8338.4277 | 552.03 |
| A5 | 3854.6654 | 24215.106 | -504.31 |
| A6 | -6681.7747 | -43107.078 | 178.56 |
| A7 | 7192.6002 | 46012.132 | |
| A8 | -4345.2612 | -27015.265 | |
| A9 | 1119.5957 | 6705.4599 | |

S3. Pore size distributions

The pore size distributions were obtained from the nitrogen adsorption isotherms at 77 K by NLDFT (non local density functional theory) model provided by NovaWin version 10.0 software.

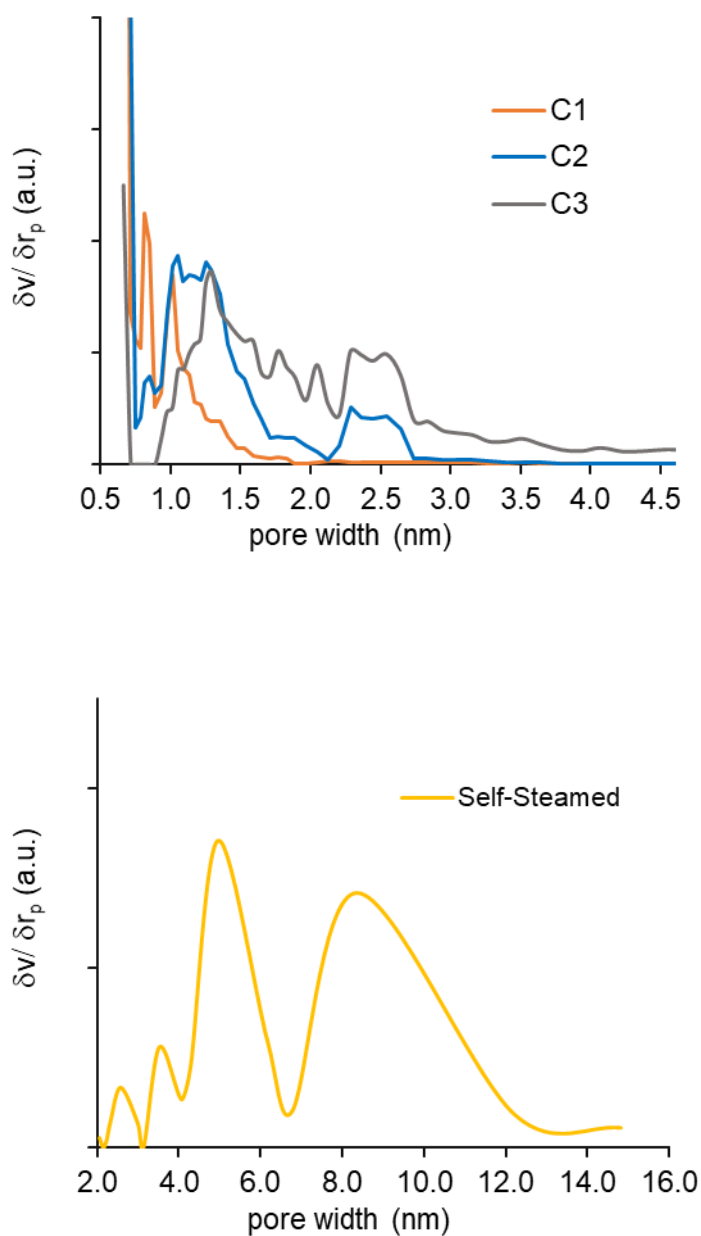
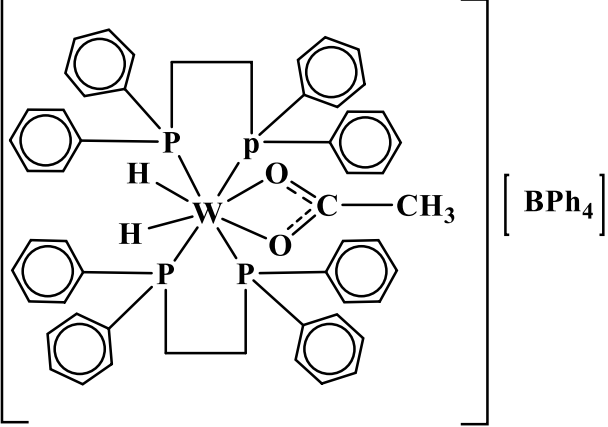
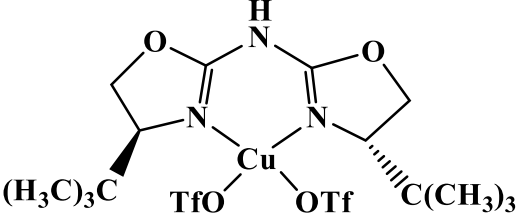
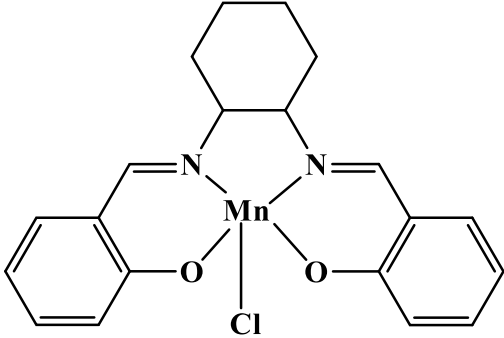
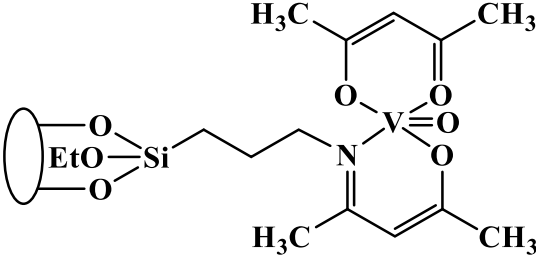


Figure S1. Pore size distributions for the carbon materials (C1, C2 and C3) and for the dealuminated Y zeolite (Self Steamed).

S4. Structures of the metallic complexes supported in different materials.

| Complex | Structure | Reference |
|---------|--|-----------|
| Comp1 |  | [5] |
| Comp2 |  | [6] |
| Comp3 |  | [7] |
| Comp4 |  | [8] |

S5. Network-accessible geometric volume.

Table S2. Network-accessible geometric volume (in cm³g⁻¹) obtained with PoreBlazer [9] for the zeolites and MOFs studied in this work.

| | | |
|----------|------------|-------|
| Zeolites | NaY | 0.362 |
| | Mordenite | 0.241 |
| | ETS-10 | 0.166 |
| MOFs | CuBTC | 0.794 |
| | UiO-66 | 0.426 |
| | MIL-53(Al) | 0.527 |
| | MIL-101 | 1.815 |

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