Electronic Supplementary Information:

Assessment of the t-plot method applied to hierarchical zeolites

In "Validity of the t-plot Method to Assess Microporosity in Hierarchical Micro/Mesoporous Materials" by Galarneau et. al. [1], an abacus has been proposed to correct the micropore volume ($V_{micro(t\text{-}plot)}/V_{micro(true)}$) in materials presenting both micropores and mesopores.

The abacus is described by the equation: $y = A + Bx^C$

and A = 0.34, B = 2.70, C = -0.59, $y = V_{micro(t\text{-}plot)}/V_{micro(true)}$ and $x = V_{micro}/V_{total(t\text{-}plot)}$ x 100.

In this abacus the percentage of microporosity has been determined by the t-plot method by using as micropore volume ($V_{micro(t\text{-}plot)}$) the value determined classically at the intercept of low-pressure linear part (blue line in **Figure 1a**) and as total volume ($V_{total(t\text{-}plot)}$) the pore volume corresponding to the first point, which departs from the linear regime after pore filling (intercept with the dashed black line in **Figure 1a**). This is in line with the classical t-plot method.

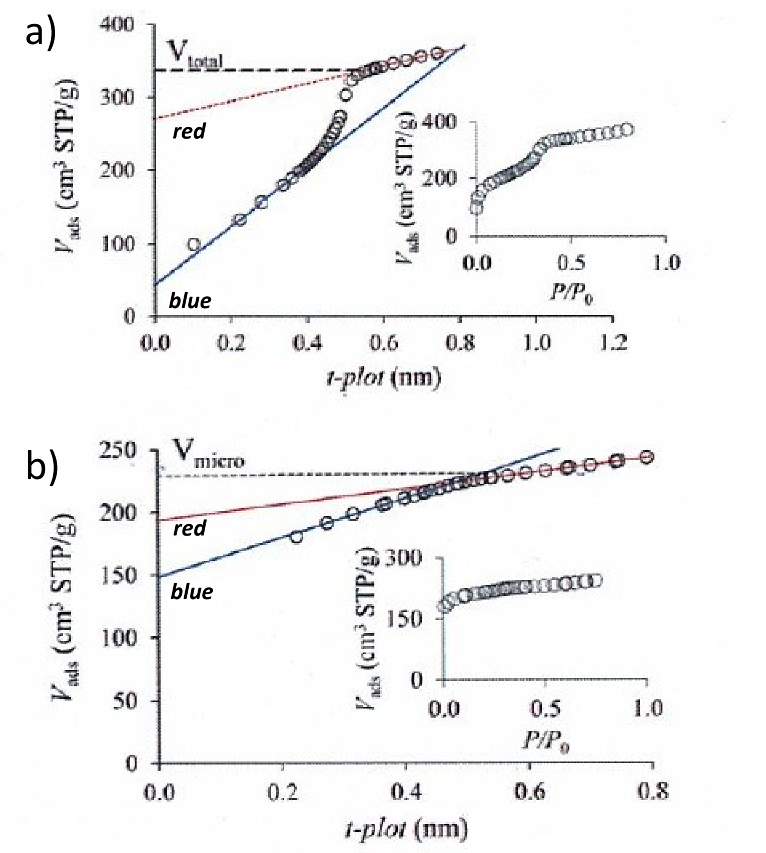

Figure 1. (a) t-plot for nitrogen adsorbed at 77 K in a mechanical mixture of 20 wt % FAU and 80 wt % Al-MCM-41 (the inset shows the nitrogen adsorption isotherm at 77 K which was used to obtain the t-plot). The intercept of the dashed black line with the y-axis provides an estimate of the total porous volume, while the intercept of the blue line provides an estimate of the microporous volume. (b) t-plot for nitrogen adsorbed at 77 K in FAU zeolite (the inset shows the nitrogen adsorption isotherm at 77 K which was used to obtain the t-plot). The blue and red lines, which correspond to linear regressions of the t-plot in different thickness ranges, provide different underestimation of the microporous volume of the sample, while the dashed black line gives the real microporous volume of the zeolite.

Galarneau et. al. described the application of the classical t-plot method as:
"The classical way to determine the microporous volume of a material by the t-plot method is to extrapolate the linear fit in the low-pressure range (blue line in **Figure 1b** for the FAU zeolite) and to take the intercept as the microporous volume. Indeed this leads to an underestimation of the correct (or true) microporous volume of the material and already proves the lack of the validity of the t-plot method applied to pure microporous solids."

It is widely reported that the t-plot is a limited model and in purely microporous materials often underestimates the true micropore volume. In addition, it is known that the presence of mesopores severely complicates the use of the t-plot. The strength of the proposed abacus is that a correction can be made to more accurately determine the micropore volume of hierarchical zeolites and/or micro/mesoporous mixtures. Yet we believe that a limitation of the t-plot persists in the determination of the micropore volume of a purely microporous material, which is used in the proposed abacus. To explain this in further detail, the theory behind the t-plot deserves elaboration.

The isotherm and t-plot on a non-porous material is set as standard and deviations from this standard t-plot (common t-curve) are described. **Figure 2** displays this standard "reference" isotherm, denoted as **(A)** and a deviation from this "reference" isotherm presented by **(B)**, which is solely the result of the presence of micropores. The t-plot of **(A)**, the non-porous reference plot, runs through the origin when extrapolated. The t-plot of **(B)**, with the added micropores, has an intercept when extrapolated. It can be seen in **Figure 2** that the extrapolation occurs at higher thickness values of the t-plot [2].

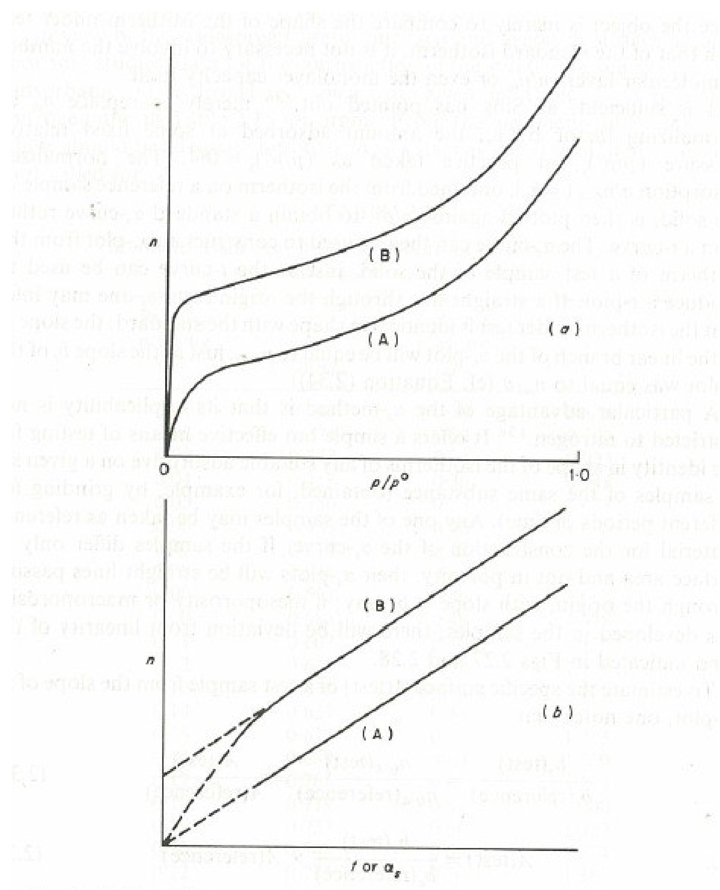

Figure 2: Effect of microporosity of the isotherm and t-plot. (a) **(A)** is the isotherm on a nonporous sample of the adsorbent; **(B)** is the isotherm of the same solid when micropores have been introduced into it. (b) t-plots corresponding to the isotherms of (a).

Up to a thickness of 0.4 nm (relative pressure (p/p_0) of ca. 0.2), the micropores (pores with diameters up to 2 nm) are still being filled. By applying the t-plot method in the range < 0.4 nm (or < 0.2 p/p_0) not all micropores may have been filled necessarily, and the slope of the line will depend of the size of the micropores present in the material. At a layer thickness of 0.4 nm (or p/p_0 = 0.2) all micropores surely have been filled. Since there is no additional porosity present in a purely microporous material, using the intercept of the red line in **Figure 1b** will give a better representation of the micropore volume compared to the use of the intercept of the blue line. In this case, applying the red line is also fully in line with the work described in **Figure 2**.

The blue line in **Figure 1a** is applied up to a thickness of approximately 0.4 nm. The micropores are completely filled at this pressure and at higher pressures the mesopores are filled. Importantly, in micro/mesoporous mixtures it is undesirable to apply the correction at higher pressures (red line) as doing so will lead to the inclusion of mesoporosity. The latter is particularly challenging in the case the mesopores are in the range of 2-4 nm (typical for MCM-41). Hence, instead of merely correcting for the underestimation of the true micropore volume, this method may result in an overestimation of the micropore volume in the solid. Therefore, the intercept of the blue line is the best representation of the micropore volume, although it may underestimate the true micropore volume. Since the micropore volume determined by de t-plot (<0.4 nm, blue line) is an important ingredient of the abacus, an underestimation of the micropore volume may occur. Therefore, although the abacus is a very useful tool, in our opinion an amendment should be made to the abacus using the t-plot application over purely microporous materials, using the theory described in Gregg and Sing, as a starting point.

References

[1] A. Galarneau, F. Villemot, J. Rodriguez, F. Fajula and B. Coasne, Langmuir, 2014, 30, 13266–13274.
[2] S. J. Gregg and K. S. W. Sing, ‘Adsorption, surface area, and porosity’, 1982, Academic Press, London.