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Specific surface area determinations for microporous/mesoporous materials: the case of mesoporous FAU-Y zeolites

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ABSTRACT: A methodology for determining from N₂ adsorption isotherms at 77 K the micropore, mesopore, and external surface areas of hierarchical microporous/mesoporous

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3 materials is described. For FAU-Y zeolite, the microporous surface area calculated using the
4
5 Rouquerol criterion and the BET equation is in accord with the geometrical surface determined
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7 by the chord length distribution method. Therefore BET surface area (S_{BET}) is well representative
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9 of micropore surface areas of microporous materials and of total surface area of
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11 microporous/mesoporous materials. Mechanical mixtures of mesoporous MCM-41 and
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13 microporous FAU-Y powders of known surface areas were used to calculate the respective
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15 surface areas by weighted linear combination and the results were compared to the values
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17 obtained by the t-plot method. The first slope of the t-plot determined the mesopore + external
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19 surface areas ($S_{\text{mes+ext}}$). The linear fit of the first slope is in general in the range $0.01 < p/p_0 < 0.17$
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21 and contains the volumes and relative pressures at which all micropores are filled ($p/p_0 > 0.10$).
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23 Overestimation of $S_{\text{mes+ext}}$ values was evident and appropriate corrections were provided.
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25 External surface areas (S_{ext}) were obtained from the second slope of the t-plot, without noting an
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27 overestimation of S_{ext} , thus allowing the determination of mesopore surface areas (S_{mes}) by
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29 difference. Micropore surface areas were calculated by subtracting $S_{\text{mes+ext}}$ from the total surface
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31 area, S_{BET} . As an example, this methodology was applied to the characterization a family of
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33 hierarchical microporous/mesoporous FAU-Y (FAUmes) synthesized from H-FAU-Y (H-Y,
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35 Si/Al = 15) using C18TAB as surfactant and different NaOH/Si ratio ($0.05 < \text{NaOH/Si} < 0.25$).
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37 By increasing the NaOH/Si ratio in synthesis of FAUmes, it was shown that as the micropore
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39 surface area decreases, the mesopore surface area increases, while the micropore + mesopore
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41 surface area remains constant. This methodology allows accurate characterization of the surface
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43 areas of microporous/mesoporous materials.
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INTRODUCTION

Microporous materials such as zeolites, metal-organic frameworks, and porous carbons are widely used in catalysis, separation, selective adsorption, and metal decontamination.^{1,2} These applications benefit from the large surface areas and small pore sizes of these materials, leading to strong interactions with the surface. However, these materials suffer from internal diffusion limitation due to the small size of their pores, which limits their efficiency.¹ In Order to increase the transport in microporous materials, mesopores have been created to produce micro-/mesoporous materials.³⁻⁷ One simple way to create mesopores in microporous zeolites consists of a post-treatment in basic medium with alkyltrimethylammonium surfactants.⁸⁻¹⁰ Such hierarchical structures retain the micropores needed for a specific application and provide improved transport properties due to the presence of mesopores. The portions of micropore and mesopore surfaces are key factors to better understand these materials, which most of the time are characterized by their specific surface areas.

There are two main tools to calculate specific surface areas from adsorption measurements: the BET equation and the t-plot method, both being subject to controversy for materials containing micropores.¹¹⁻¹⁶ The t-plot method is a widely used procedure to estimate the total surface area as well as the external surface area of materials. In this method, the average thickness of an adsorbed film is first determined for a reference material containing no porosity, or only macroporosity, and having the same surface chemistry as the studied porous material. Then the so-called t-plot is created by plotting the adsorbed volume at a given pressure against the average thickness of the adsorbate film (t) obtained at the same pressure for the non-porous

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3 reference material.^{15,16} For mesoporous materials, the adsorbed volume (V) varies linearly with
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5 the film thickness (t) and passes through the origin. The total surface area (S_{tot}) is directly given
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7 by the slope of the first linear fit at low pressure with $V = S_{\text{tot}} t$. Once all pores are filled,
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9 adsorption occurs only on the external surface of the material and leads to a second linear fit at
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11 high pressure, the slope of which allows the determination of the external surface (S_{ext}) with $V =$
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13 $S_{\text{ext}} t$.
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17 For materials containing micropores, the first linear fit of the t-plot at low pressure most
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19 of the time does not pass through the origin or is not linear at very low pressure.¹⁵ The first linear
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21 fit is done using several data points and the intercept with the Y-axis is usually taken to be the
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23 micropore volume. However, it was demonstrated experimentally in a previous publication¹² that
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25 the t-plot method underestimates the micropore volume when it exceed more than 10% of the
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27 total pore volume. By modeling, it also was highlighted that the t-plot method overestimates the
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29 surface areas of hierarchical microporous/mesoporous materials, such as mesoporous MOF
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31 structures (CuBTC).¹³ One goal of the present study is to verify experimentally this observation
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33 of overestimation of surface area by t-plot analysis.
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38 To analyze carefully micropore and mesopore surface areas in a material by the t-plot
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40 method, it is of prime importance to use a good reference isotherm with the same surface
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42 chemistry as the analyzed materials. Different models of film thickness (e.g., Harkins and Jura,
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44 Halsey, Lecloux, etc) have been proposed in the literature.¹⁶ But none of them are accurate for
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46 porous silica. As shown previously for purely mesoporous MCM-41 silica with a mesopore
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48 diameter of 4 nm, the t-plots do not pass through the origin.¹² Consequently, reference isotherms
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50 for materials of similar surface chemistry first need to be established. Toward this end, reference
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52 isotherms have been recorded for different types of non-porous¹² and macroporous silica¹⁷ and all
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54 of them are available for t-plot analysis of porous silica-based materials.
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3 Another way to calculate total surface area is to fit the adsorption data to the BET
4 equation. This is a routine characterization technique for porous materials.^{11,14-16} The BET
5 specific surface area (S_{BET}) is usually assessed from adsorption experiments prior to capillary
6 condensation of the fluid. The hypothesis of the BET model is that (1) adsorption occurs on
7 energetically homogeneous sites and (2) molecules can adsorb on each other.^{11,14-16} In this case,
8 the adsorption energy for all molecules adsorbed above the first layer is constant and equal to the
9 cohesion energy in the bulk liquid. The pressure range used to estimate the BET surface should
10 follow the Rouquerol criterion,^{11,14,15,18} which makes use of the adsorption data up to the p/p_0
11 pressure where $V(1-p/p_0)$ exhibits a maximum. Adsorption beyond this value represents the point
12 where the adsorbed amount increases less rapidly with pressure in comparison to the first
13 adsorbed layer.¹⁵

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28 The resulting monolayer capacity V_m obtained from the BET plot provides a reasonable
29 estimate of the geometrical surface when V_m is converted to surface area using the common value
30 of 0.162 nm^2 for the molecular cross section of nitrogen.¹⁵ However, care should be taken when
31 using this approach. Depending on the surface chemistry of the material, the ovoid nitrogen
32 molecules can pack differently on the surface. The effective cross sections for nitrogen, for
33 instance, can vary from 0.135 nm^2 for hydroxylated silica surfaces to 0.162 nm^2 for
34 hydrophobic surfaces.¹⁹

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The present study is in two parts. The first part concerns the use of the BET equation and
the t-plot method to assess surface areas for micro-/mesoporous materials. The surface area
determined by the BET equation for microporous FAU-Y zeolite is compared to the geometrical
calculation of the surface by chord length distribution. The surface areas for micro-/mesoporous
samples are compared to the areas determined by linear combination of the adsorption data for
mechanical mixtures of FAU-Y and MCM-41 with known micropore and mesopore surface

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3 areas, respectively. A methodology is proposed to decouple the micropore, mesopore and
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5 external surface areas of the materials.
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8 In the second part of this study, the corrected surface areas determined from the t-plots of
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10 mechanical mixtures of MCM-41 and FAU-Y are used to obtain the micropore and mesopore
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12 surfaces of a family of hierarchical micro-/mesoporous FAU-Y materials (denoted FAUmes)
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14 synthesized by post-treatment of FAU-Y in presence of octadecyltrimethylammonium (C18TAB)
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16 surfactant in basic medium at different NaOH/Si ratios ($0.05 < \text{NaOH/Si} < 0.25$).
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21 **EXPERIMENTAL SECTION**

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26 **Synthesis of mesoporous FAU-Y (FAUmes).** In a beaker (250 mL), x g of NaOH pellets
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28 ($x = 0.199 - 1.998$ g) was added to 180 g of H₂O and the mixture was magnetically stirred until
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30 complete dissolution at room temperature (25 °C). Then 7.843 g of octadecyltrimethylammonium
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32 bromide (C18TAB) was added and stirring was continued until dissolution was again complete.
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34 The magnetic stirrer was then replaced by an endless screw stirrer, which is more gentle and
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36 necessary to keep the particle size and shape of the initial particles. The endless screw stirrer was
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38 described previously for the pseudomorphic transformation of silica particles into MCM-41
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40 particles.²⁰ Then 12g of the parent dealuminated H-FAU-Y zeolite (Si/Al = 15), obtained from
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42 Zeolyst under the trade name CBV720, was then added and the mixture stirred for 1-2 h at room
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44 temperature (25 °C) to obtain a homogeneous white suspension. The suspension was then
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46 transferred into a Teflon-lined stainless-steel autoclave (250 mL) and kept under static conditions
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48 for 20 hours at 115 °C. The resulting mixture was then filtered and washed with water until
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50 neutral pH. The sample was dried in an oven at 80 °C for 12 h and calcined at 550 °C for 8 h
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3 (heating rate 5 °C/min). The molar ratios of the reaction mixtures were 1.0 FAU-Y / 0.10
4 C18TAB / n NaOH / 50 H₂O ($n = 0.025 - 0.25$).
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7 **Synthesis of MCM-41.** Al-MCM-41(C16, Si/Al = 15), used in the preparation of
8 mechanical mixtures of FAU-Y and MCM-41, was synthesized as follows. NaAlO₂ (Carlo Erba)
9 was added to an alkaline solution containing cetyltrimethylammonium bromide surfactant
10 (C16TAB) (Aldrich). The mixture was stirred at 50 °C until complete dissolution before adding
11 Aerosil 200 silica (Degussa) and stirring for 1 h. The composition of the mixture in molar ratio is
12 1 SiO₂ / 0.07 NaAlO₂ / 0.1 C16TAB / 0.25 NaOH / 50 H₂O. The slurry was then placed in a
13 stainless-steel autoclave and heated at 115 °C for 24 h. The resulting material was then filtered
14 and washed until neutral pH, dried at 80 °C, and calcined at 550 °C for 8 h under air-flow.
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26 **Materials Characterization.** N₂ adsorption isotherms at 77 K were measured on a
27 Belsorb apparatus using 200-300 mg samples outgassed in vacuum at 250 °C for 12 h before
28 analysis. Ar adsorption isotherms at 87 K were obtained on a Quantachrome Autosorb-1C
29 apparatus. The 50-mg samples were outgassed under vacuum at 200 °C for 20 h before analysis.
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38 **RESULTS AND DISCUSSION**

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42 **Surface areas of FAU-Y and MCM-41.** The nitrogen sorption isotherms at 77 K of FAU-Y and
43 MCM-41 are reported in [Figure 1](#) and t-plot curves are provided in [Figure 2](#). The surface areas of
44 FAU-Y and MCM-41 were determined using the BET equation and the t-plot method.
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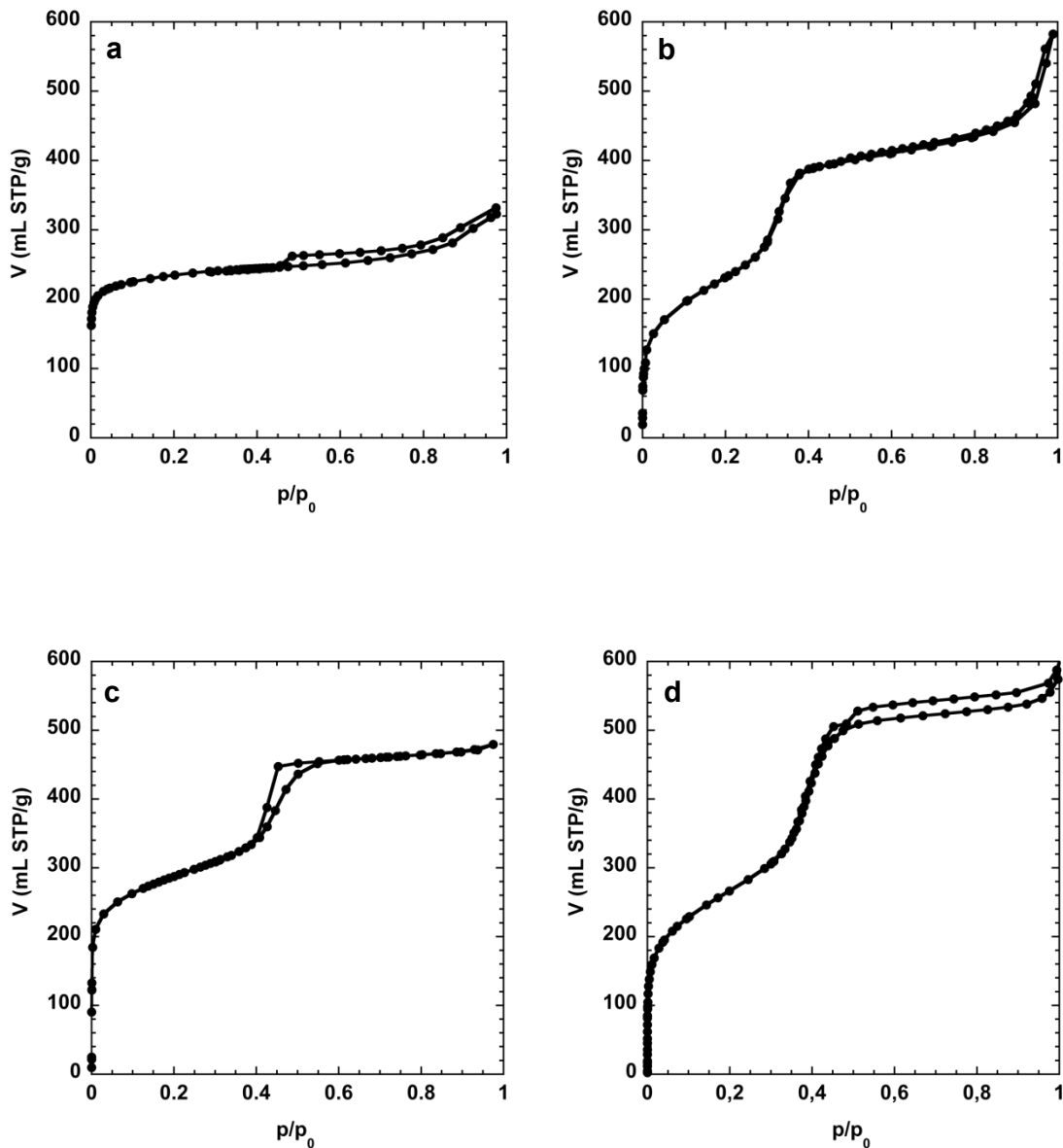


Figure 1. Nitrogen sorption isotherms at 77 K of (a) H-FAU-Y (Si/Al = 15) (CBV720), (b) Al-MCM-41(C16) (Si/Al = 15) and hierarchical microporous/mesoporous Na-FAU-Y (Si/Al = 15), named FAUmes, synthesized from H-FAU-Y and C18TAB surfactant with different NaOH/Si ratio (c) FAUmes – NaOH/Si = 0.10 and (d) FAUmes – NaOH/Si = 0.25.

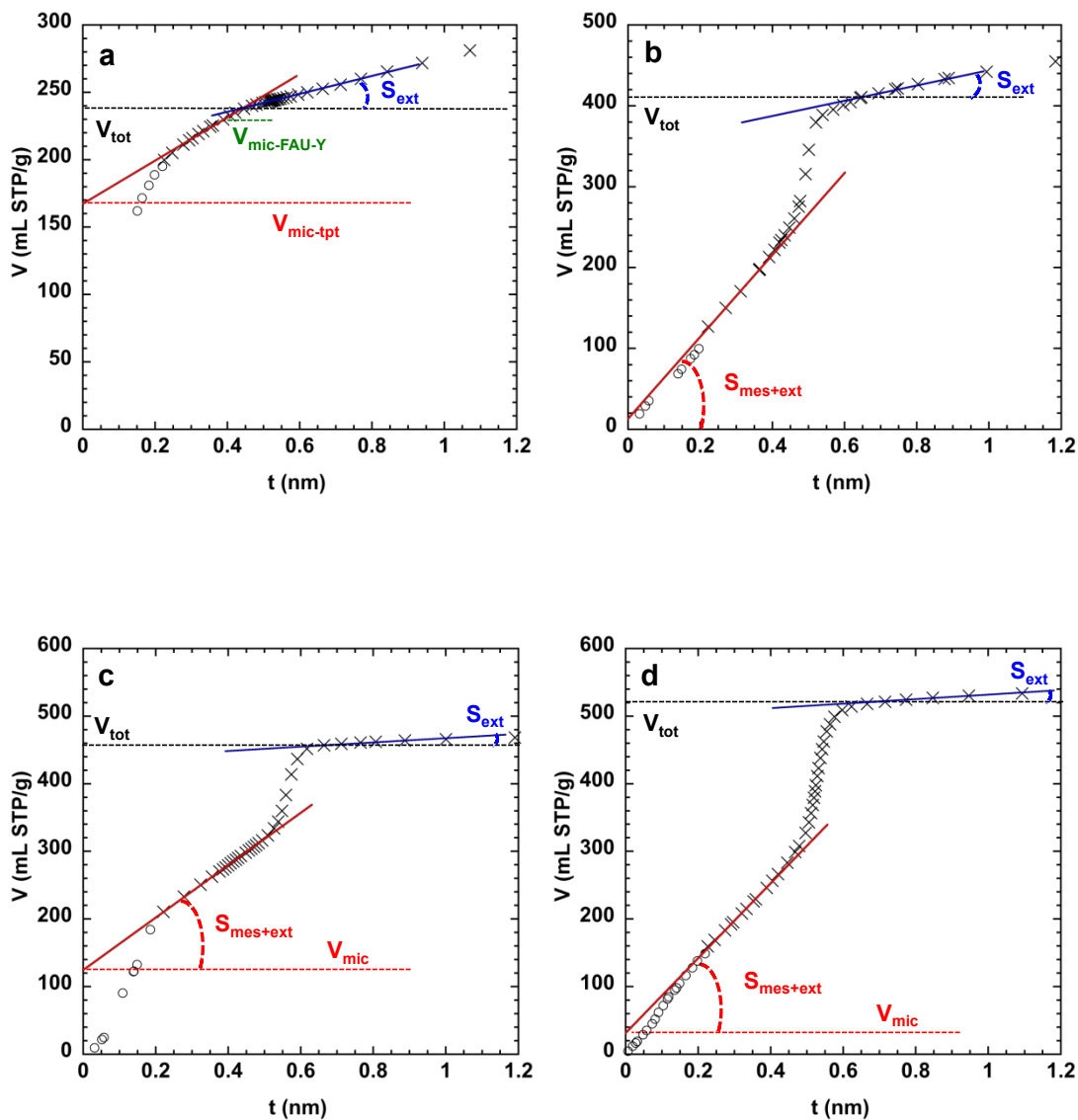


Figure 2. t-plot curves of (a) H-FAU-Y (Si/Al = 15) (CBV720), (b) Al-MCM-41(C16) (Si/Al = 15) and hierarchical microporous/mesoporous Na-FAU-Y (Si/Al = 15) synthesized from H-FAU-Y and C18TAB surfactant with different NaOH/Si ratio (c) FAUmes(C18) – NaOH/Si = 0.10 and (d) FAUmes(C18) – NaOH/Si = 0.25. t-plots were produced using (crosses) Aerosil 200 as reference isotherm and fitted by Eq. 5-7 for the pressure range $0.01 < p/p_0 < 0.80$. For the low

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3 pressure range ($p/p_0 < 0.01$) t-plots were produced using (circles) LiChrospher 1000 (Si1000) as
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5 reference isotherm described by Jaroniec et al.¹⁷ (see supporting informations for the equations).
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12 The BET surface areas have been calculated using the Rouquerol criterion.¹¹ The Rouquerol plot,
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14 which is $V(1-p/p_0)$ as a function of p/p_0 , has been plotted to identify the first maximum pressure
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16 useful for a linear fit to the BET equation (Eq. 1).
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$$\frac{p/p_0}{V(1-p/p_0)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} (p/p_0) \quad (1)$$

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27 The adsorption data are then fit to the BET equation (Eq. 1) by a linear regression ($y = ax + b$).
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29 The slope a and the intercept b are used to calculate the monolayer volume (V_m) and then the
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31 BET surface area (S_{BET}) with the following equations (Eq. 2,3):
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$$V_m = 1/(a+b) \quad (2)$$

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$$S_{BET} = \sigma_{N_2} \frac{V_m}{V_{N_2}} N_A \quad (3)$$

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45 where V_{N_2} is the molar gas volume, N_A is Avogadro number, and σ_{N_2} is the cross-section of the
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47 N_2 molecule, which corresponds experimentally to (Eq. 4) for $\sigma_{N_2} = 0.162 \text{ nm}^2$:
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$$S_{BET} (\text{m}^2/\text{g}) = 4.36 V_m (\text{mL STP}) \quad (4)$$

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3 For MCM-41, the BET surface area was 843 m²/g.
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5 The use of BET equation for microporous materials surface analysis is subject to
6 controversy. However, computational studies of hierarchical micro-/mesoporous MOF materials
7 (e.g., CuBTC) demonstrated that the BET surface area is well representative of the total surface
8 area (micropore + mesopore + external surface areas). Moreover, the BET surface area is in
9 agreement with the accessible surface area calculated by chord length distribution ($S_{\text{chord}} = 2187$
10 m²/g and $S_{\text{BET}} = 2108$ m²/g),¹⁸ provided the Rouquerol criterion is respected. Similar results have
11 been obtained for a purely microporous MOF ($S_{\text{chord}} = 1979$ m²/g and $S_{\text{BET}} = 1958$ m²/g).¹⁸ it is
12 therefore possible to use a BET calculation to determine the total surface area for materials
13 containing microporosity.
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26 The nitrogen isotherm at 77 K for FAU-Y has been recorded (Figure 1) and the BET
27 surface area has been calculated taking into account the Rouquerol criterion. S_{BET} for FAU-Y is
28 937 m²/g. This value is close, but slightly lower than the accessible total surface area of FAU-Y
29 calculated by computational chord length distribution ($S_{\text{chord}} = 1259$ m²/g). The reported surface
30 area of FAU-Y accessible to water molecules (0.28 nm kinetic diameter) is 1211 m²/g, in
31 accordance with the chord length distribution calculation of this study.²¹ The experimentally
32 calculated S_{BET} from the N₂ isotherm is lower ($S_{\text{BET}} = 937$ m²/g), which can be explained by the
33 use of the larger nitrogen molecule (0.364 nm kinetic diameter).
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44 The BET surface area of FAU-Y was also determined from Ar isotherms at 87 K ($S_{\text{BET}} =$
45 821 m²/g). This latter value is lower than the one obtained with N₂. Ar has a similar kinetic
46 diameter (0.34 nm) as N₂,²² but Ar is a globular nonpolar molecule that leads essentially to non-
47 specific interactions with all types of adsorbents. On the other hand, N₂ has a particular ovoid
48 shape and is quadrupolar, leading to specific interactions with hydroxylated surfaces. One
49 hypothesis is that the ovoid shape of N₂ allows nitrogen to partially enter the sodalite cages
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3 (window aperture approx. 0.28 nm). Argon apparently only probes the supercages of FAU-Y
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5 (window aperture 0.74 nm). Thus, the total micropore + external surface area of FAU-Y, as
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7 determined using the BET equation, is 937 m²/g and 821 m²/g, respectively, when nitrogen and
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9 argon are used as adsorbates.
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12 The second way to calculate the surface areas of porous materials is by the t-plot method,
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14 which plots the volume adsorbed as a function of the thickness (t) of the adsorbed film.^{15,16} In
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16 order to obtain accurate t-plot curves, the choice of a reference isotherm with a surface chemistry
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18 similar to the studied material is essential. A non-porous silica (Aerosil-200) was used in this
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20 study as a reference isotherm over the partial pressure range 0.009 < p/p₀ < 0.80. For this range of
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22 pressure, the Aerosil 200 reference isotherm is in good agreement with the reference isotherms
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24 reported by Jaroniec *et al.*¹⁷ for the macroporous silica LiChrospher Si-1000, as well as other
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26 forms of standard adsorption isotherms.¹⁷ For our study, the Aerosil 200 reference isotherm was
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28 fit by parts to Eqs. 5-7 below. In comparison to the fitting procedure we reported in a previous
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30 publication,¹² the present fitting results were in better agreement with the data presented by
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32 Jaroniec *et al.*¹⁷ These new fits were preferred for this study.
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37 Equations 5-7 were used to transform p/p₀ into adsorbate layer thickness t:

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42 0.009 < p/p₀ < 0.12

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$$t = 1.62973 + 76.4748 (p/p_0) - 2171.7914 (p/p_0)^2 + 41734.77357 (p/p_0)^3 - 465290.41181 (p/p_0)^4 +$$

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$$2.72432 \cdot 10^6 (p/p_0)^5 - 6.43708 \cdot 10^6 (p/p_0)^6 \quad (5)$$

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51 0.13 < p/p₀ < 0.60

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$$t = 3.07721 + 5.64019 (p/p_0) \quad (6)$$

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3 $0.60 < p/p_0 < 0.80$
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5 $t = 4592.05803 - 38117.31548 (p/p_0) + 131602.19741 (p/p_0)^2 - 241680.40239 (p/p_0)^3 +$
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7 $249079.8569 (p/p_0)^4 - 136632.44762 (p/p_0)^5 + 31182.4149 (p/p_0)^6$ (7)
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12 In order to obtain mesopore + external surface areas ($S_{mes+ext}$), the first linear t-plot fit was
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14 carried out at low t with the equation:
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19 $S(m^2/g) = \text{Slope}/(\rho_{N_2gas}/\rho_{N_2liq})$ (8)
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24 corresponding experimentally to:
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28 $S(m^2/g) = (\text{Slope}/646) 10^4$ (9)
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33 For external surface area determinations (S_{ext}), the second linear fit of the t-plot (Figure 2) was
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35 performed at t below 0.92 nm; that is, at pressures below $p/p_0 = 0.8$ where the domain of validity
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37 is observed for the t-plot curve obtained for Aerosil-200. S_{ext} is calculated from the slope of the
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39 second linear fit at high t (Eq. 9).
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42 The t-plot curve of MCM-41 shows two slopes (Figure 2), one before the condensation
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44 step due to mesopore filling and one after due to the adsorption on the external surface. The first
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46 slope represents the total surface area (mesopore + external surface), which is equivalent to BET
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48 the surface area for mesoporous materials, and the second slope at high pressure represents the
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50 external surface area. The mesopore surface area is calculated by difference between the total
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52 surface area and the external surface area. This can be done by two ways: the subtraction of the
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54 external surface area from the total surface area determined by (i) the BET equation or (ii) by the
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3 t-plot. The total pore volume (or mesopore volume in the case of MCM-41) is obtained when the
4 experimental points start being inferior to the second linear fit of the t-plot at high pressure (high
5 t, **Figure 2**). The external surface of MCM-41 is 143 m²/g. A good correlation was found for
6 MCM-41 between BET surface area (843 m²/g) and mesopore + external surface area (823 m²/g)
7 determined by t-plot. The error in surface area determination is therefore ± 20 m²/g or around 2.5
8 % of the measured surface areas. The mesopore surface (S_{mes}) of MCM-41 is then calculated by
9 difference between S_{BET} and S_{ext} ($S_{mes} = 700$ m²/g) or between $S_{mes+ext}$ and S_{ext} ($S_{mes} = 680$ m²/g).
10 The total or mesopore volume of MCM-41 ($V = 0.66$ mL/g) was taken as the point where the
11 second slope of the t-plot departs from the experimental data (**Figure 2**).
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24 In order to calculate the micropore surface area of FAU-Y, the external surface was first
25 determined from the t-plot. The use of t-plot method for calculating the surface areas of
26 microporous materials is subject to controversy^{13,15} and only external surface area calculation is
27 recommended using the fit at high pressure (or high film thickness).¹⁵ T-plot of FAU-Y was
28 determined (**Figure 2**) and S_{ext} for FAU-Y was calculated (85 m²/g). The micropore surface (S_{mic})
29 of FAU-Y was then obtained by the difference between S_{BET} and S_{ext} , which provided the value
30 $S_{mic} = 852$ m²/g. The micropore volume of FAU-Y is difficult to assess by the t-plot method due
31 to the compressibility of nitrogen in micropores,¹⁵ which, contrary to nitrogen in mesopores,
32 leads to a non-constant nitrogen film thickness for a given pressure. The thickness of the film
33 increases with decreasing micropore diameter.¹⁵ For materials containing micropores, the
34 intercept of the first slope with the Y-axis usually is used to determine the micropore volume. But
35 as shown by computational studies for pure microporous or micro-/mesoporous materials, t-plots
36 underestimate micropore volumes¹⁵ and overestimate surface areas.¹³ The underestimation of
37 micropore volume by t-plot method has been demonstrated experimentally for materials
38 containing more than 10% micropore volume.¹² For dealuminated FAU-Y, it is also difficult to
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3 measure exactly the micropore volume by t-plot as a few small mesopores (2- 4 nm) arise in the
4 material through dealumination, leading to additional volume. However the examination of the
5 nitrogen adsorption at very low pressure expressed as $\log(p/p_0)$ (Figure S1) allows better
6 identification of these small mesopores. The micropore volume (V_{mic}) of FAU-Y has been
7 assumed to be filled completely at $p/p_0 = 0.1$ ($V_{mic} = 0.317$ mL/g). Thus, the intercept of the first
8 slope of the t-plot with the Y-axis (Figure 2) for this purely microporous material is misleading,
9 because it corresponds instead to the underestimated value of $(V_{mic})_{tpt} = 0.232$ mL/g.¹²

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12 By careful use of BET equations and t-plot methods, it was possible to assess the different
13 surface areas for purely mesoporous materials and purely microporous materials. For mesoporous
14 MCM-41, the two types of surface areas were $S_{mes} = 680-700$ m²/g and $S_{ext} = 143$ m²/g, whereas
15 for FAU-Y, surface areas were $S_{mic} = 852$ m²/g and $S_{ext} = 85$ m²/g.

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31 **Surface areas of mechanical mixtures of FAU-Y and MCM-41.** As said previously, for micro-
32 /mesoporous materials, it has been shown by modeling that the t-plot method overestimates
33 surface areas.¹³ To experimentally verify this conclusion, mechanical mixtures with different
34 weighted portions of FAU-Y and MCM-41 with known micropore and mesopore surfaces,
35 respectively, have been prepared by simple powders mixing without grinding and analyzed by
36 nitrogen adsorption at 77 K. The micropore and mesopore surface areas of the mixtures have
37 been calculated independently by linear combination and compared to the results of the t-plot
38 analysis (Figures 3, S3).

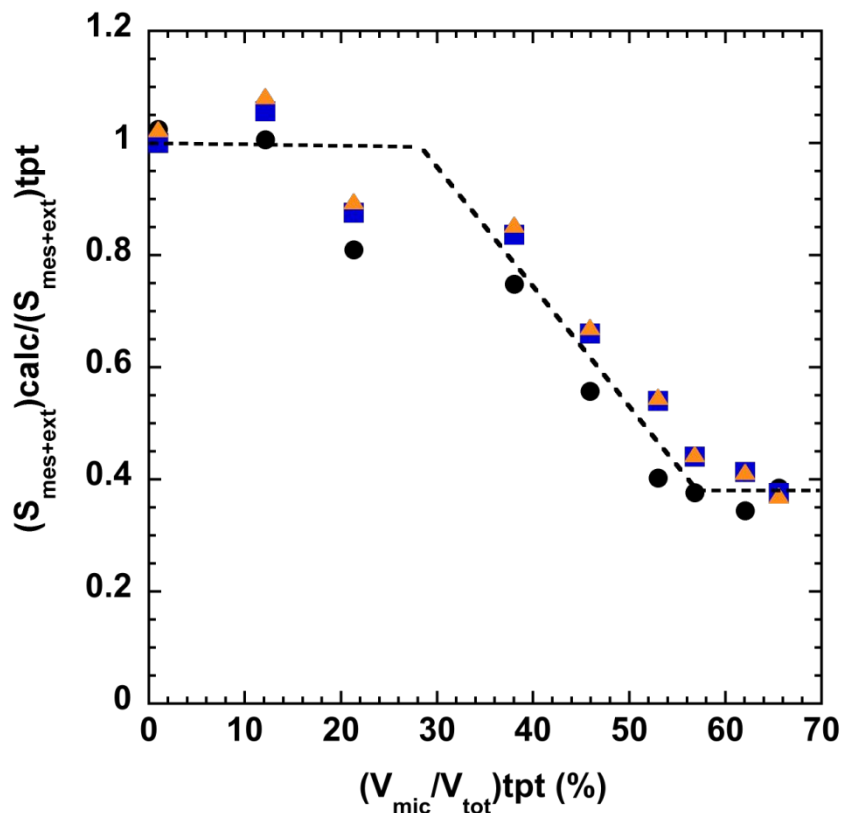


Figure 3. For mechanical mixtures of MCM-41 and FAU-Y, comparison of mesopore + external surface areas $S_{mes+ext}$ determined by t-plot method $(S_{mes+ext})_{tpt}$ and calculated by linear combination $(S_{mes+ext})_{calc}$ as a function of the ratio of micropore volume to total pore volume determined by t-plot $(V_{mic}/V_{tot})_{tpt}$. $(S_{mes+ext})_{calc}$ were determined by 3 different ways: (1) by subtracting the weighted micropore surface of FAU-Y from S_{BET} of the mixture (circles), (2) by adding the weighted S_{ext} of the mixture to the weighted mesoporous surface S_{mes} of MCM-41 calculated either from (i) $S_{BET} - S_{ext}$ (triangles) or (ii) from $S_{mes+ext} - S_{ext}$ (squares). The dashed line represents the fits of these points, which will be used to correct the $(S_{mes+ext})_{tpt}$ of hierarchical microporous/mesoporous FAU-Y (FAUmes) materials.

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3 The external surface areas (S_{ext})_{calc} and the mesopore + external surface areas
4 ($S_{\text{mes+ext}}$)_{calc} of the mechanical mixtures of MCM-41 and FAU-Y were first calculated by
5 weighted linear combination of the two types of surface areas. The “calculated” mesopore +
6 external surface areas, ($S_{\text{mes+ext}}$)_{calc}, were determined in three different ways: (1) by subtracting
7 the weighted micropore surface of FAU-Y from the total surface S_{BET} of the mixture (Figures 3,
8 S3, circles), (2) by adding the weighted S_{ext} of the mixture to the weighted mesoporous surface
9 S_{mes} of MCM-41 calculated either from (i) $S_{\text{BET}} - S_{\text{ext}}$ (Figures 3, S3, triangles) or (ii) from $S_{\text{mes+ext}} -$
10 S_{ext} (Figures 3, S3, squares). All of these approaches to calculate ($S_{\text{mes+ext}}$)_{calc} for the mechanical
11 mixtures are in good agreement (Figures 3, S3). The slightly lower values of ($S_{\text{mes+ext}}$)_{calc}
12 calculated by method 1 (Figures 3, S3, circles) are due to a small contribution of the mesopore
13 surface in S_{mic} of FAU-Y due to the fact that FAU-Y is a dealuminated zeolite and contains a
14 small volume (0.036 mL/g) of small mesopores (diameter between 2 – 4 nm).
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30 For the mechanical mixtures of FAU-Y and MCM-41, the mesopore + external surface
31 areas ($S_{\text{mes+ext}}$)_{tpt} and micropore volumes (V_{mic})_{tpt} were then determined from the first linear fit
32 of the t-plot at low t (Figure S2). The linear fit of the first slope is in general in the range $0.01 <$
33 $p/p_0 < 0.17$, corresponding to $0.2 < t < 0.4$ nm, and contains the volumes and relative pressures at
34 which all micropores are filled (*ie.* $p/p_0 > 0.10$, corresponding to $t > 0.36$ nm). The micropore
35 volume (V_{mic})_{tpt} was obtained from the intercept of the first linear fit (low t) with the Y-axis and
36 ($S_{\text{mes+ext}}$)_{tpt} was calculated from the slope of this first fit (low t) with Eq. 9. The external surface
37 area (S_{ext})_{tpt} was determined using Eq. 9 and the second linear fit of the t-plot (Figure S2)
38 performed at high t below 0.92 nm. The second linear fit corresponded to pressures below $p/p_0 =$
39 0.8 where the domain of validity was observed for the t-plot curve for the Aerosil-200 silica
40 reference.
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The comparison between t-plot analysis for $(S_{\text{ext}})_{\text{tpt}}$ and $(S_{\text{mes+ext}})_{\text{tpt}}$, and linear combination calculations for $(S_{\text{ext}})_{\text{calc}}$ and $(S_{\text{mes+ext}})_{\text{calc}}$ (Figures 3 and S3), reveals that the values for the external surface areas are equivalent. Although there is no overestimation of external surface areas by t-plot analysis (Figure S3), the $S_{\text{mes+ext}}$ determined by t-plot $(S_{\text{mes+ext}})_{\text{tpt}}$ overestimates the “calculated” value of $S_{\text{mes+ext}}$ ($(S_{\text{mes+ext}})_{\text{calc}}$) determined by linear combination for materials presenting a micropore surface area higher than 200 m²/g (Figures 3 and S3).

To better quantify the overestimation of $(S_{\text{mes+ext}})_{\text{tpt}}$ by the t-plot method, the ratio $(S_{\text{mes+ext}})_{\text{calc}}/(S_{\text{mes+ext}})_{\text{tpt}}$ was represented as a function of the fraction of micropore volume $(V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}}$ contained in the mechanical mixtures as determined by t-plot $((V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}})$ (Figure 3). As explained previously, the total pore volume (V_{tot}) was taken from the t-plot (Figure S2) when the second fit (high t) deviates from the experimental points as previously demonstrated by modeling.¹⁵ The micropore volume is given by the intercept of the first fit of the t-plot (low t) with the Y-axis (Figure S2). The highest ratio $(V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}}$ observed by t-plot is for pure FAU-Y and corresponds to $(V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}} = 70\%$, not 100% due to the underestimation of micropore volume.¹² As a result, this graph (Figure 3) shows that the t-plot method gives accurate results for $S_{\text{mes+ext}}$ ($(S_{\text{mes+ext}})_{\text{calc}} = (S_{\text{mes+ext}})_{\text{tpt}}$) for materials containing less than 30% of micropore volume ($0 < (V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}} < 30\%$). For larger amounts of micropore volume, $S_{\text{mes+ext}}$ is overestimated by the t-plot method, and the overestimation increases linearly with increase in the micropore volume until a maximum is reached $(V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}} > 55\%$ (Figure 3).

The following equations (Eq. 10 – 12) have are provided to correct $(S_{\text{mes+ext}})_{\text{tpt}}$ determined by t-plot method for microporous/mesoporous materials:

$$(V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}} < 30\%: \quad (S_{\text{mes+ext}})_{\text{calc}} / (S_{\text{mes+ext}})_{\text{tpt}} = 1 \quad (10)$$

$$30 < (V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}} < 55\%: \quad (S_{\text{mes+ext}})_{\text{calc}} / (S_{\text{mes+ext}})_{\text{tpt}} = 1.6 - 0.02138 (V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}} \quad (11)$$

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3 $(V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}} > 55\%:$ $(S_{\text{mes+ext}})_{\text{calc}} / (S_{\text{mes+ext}})_{\text{tpt}} = 0.38$ (12)
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7 with $(V_{\text{mic}}/V_{\text{tot}})_{\text{tpt}}$ expressed in %.
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12 **Surface areas of a family of hierarchical mesoporous FAU-Y.** In order to improve transport
13 properties of zeolite crystals mesopores can be created.¹⁻¹⁰ In 2005, an attractive procedure was
14 proposed consisting of the transformation of a silica-rich FAU-Y into mesoporous FAU-Y by a
15 post-treatment in an alkaline solution containing alkyltrimethylammonium bromide surfactants
16 (CnTAB). This created homogeneous ordered mesopores as in MCM-41 materials inside the
17 FAU-Y crystals.⁸⁻¹⁰ In the present study, mesoporous FAU-Y materials (named FAUmes) were
18 synthesized using C18TAB surfactant with different NaOH/Si ratio ($0.025 < \text{NaOH/Si} < 0.25$).
19 Their nitrogen isotherms at 77 K have been performed (Figure 1) and their BET surface areas and
20 t-plots have been analyzed (Figures 2 and S4) to calculate their external, micropore and
21 mesopores surface areas taking into account the corrections of $(S_{\text{mes+ext}})_{\text{tpt}}$ (Eq. 10 -12) provided
22 by the results for mechanical mixtures of FAU-Y and MCM-41.
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37 $(S_{\text{mes+ext}})_{\text{tpt}}$ surface areas were calculated from the slope (Eq. 9) of the first linear fit of the
38 t-plot. The linear fit of the first slope was in general in the range $0.01 < p/p_0 < 0.17$
39 (corresponding to $0.2 < t < 0.4$ nm) and contains the volumes and relative pressures at which all
40 micropores are filled (*ie.* $p/p_0 > 0.10$, corresponding to $t > 0.36$ nm) (Figures 2, S4). $(V_{\text{mic}})_{\text{tpt}}$
41 micropore volumes were measured at the intercept of the Y-axis with this first linear fit. $(S_{\text{ext}})_{\text{tpt}}$
42 surface areas were calculated from the slope (Eq. 9) of the second linear fit. The linear fit of the
43 second slope was in general in the range $0.65 < p/p_0 < 0.82$ (corresponding to $0.7 < t < 0.9$ nm)
44 and contains the volumes and relative pressures below $p/p_0 < 0.80$ (corresponding to $t < 0.92$
45 nm), where the domain of validity was observed for the t-plot curve for the Aerosil-200 silica
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3 reference. The total pore volumes ($V_{\text{tot}}\text{tpt}$) were taken from the second linear fit of the t-plot
4 where it leaves the experimental data points (Table 1). The above equations (Eq. 10-12) have
5 been applied to ($S_{\text{mes+ext}}\text{tpt}$) to obtain corrected values named ($S_{\text{mes+ext}}\text{cor}$) (Table 1).
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10 The transformation of FAU-Y into FAUmes depends of the NaOH/Si ratio used in the
11 synthesis. The step at p/p_0 around 0.4 in the nitrogen isotherms (Figure 1) is characteristic of the
12 formation of ordered mesopores of ca. 4 nm in the materials due to micelle-templating. This step
13 is observed for $0.0625 < \text{NaOH/Si} < 0.25$ revealing the transformation of FAU-Y into FAUmes
14 for this range of NaOH/Si ratio. Too low NaOH/Si ratio, such as $\text{NaOH/Si} = 0.05$, does not allow
15 for the transformation into FAUmes. External surface areas for FAU-Y and untransformed FAU-
16 Y ($0 < \text{NaOH/Si} < 0.05$) were around $100 \text{ m}^2/\text{g}$ and decrease to ca. $30 \text{ m}^2/\text{g}$ for FAUmes (0.0625
17 $< \text{NaOH/Si} < 0.25$). Initial FAU-Y particles are built by an aggregation of crystals of different
18 size and morphology around $1 \mu\text{m}$ diameter forming aggregates of ca. $10 \mu\text{m}$. The transformation
19 of FAU-Y into FAUmes occurs also in between the crystal aggregates and on the outer surface
20 the crystals leading to a slight increase of particles diameter of ca. $30 \mu\text{m}$ ²³ and, therefore, to a
21 decrease of external surface areas by a factor 3 to 4. Mesopore surface areas ($S_{\text{mes}}\text{cor}$) have been
22 calculated by difference between corrected $S_{\text{mes+ext}}$ surface areas ($S_{\text{mes+ext}}\text{cor}$) and external surface
23 areas ($S_{\text{ext}}\text{tpt}$): $(S_{\text{mes}}\text{cor}) = (S_{\text{mes+ext}}\text{cor}) - (S_{\text{ext}}\text{tpt})$ (Table 1).
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42 To assess micropore surface areas of FAUmes materials by subtracting ($S_{\text{mes+ext}}\text{cor}$) from
43 the total surface area, the total surface areas of the materials have been calculated by BET
44 equation (S_{BET}) using the Rouquerol criterion¹¹ (Figures 4, S5) to determine the highest p/p_0
45 pressure to use in the fit of the BET equation.
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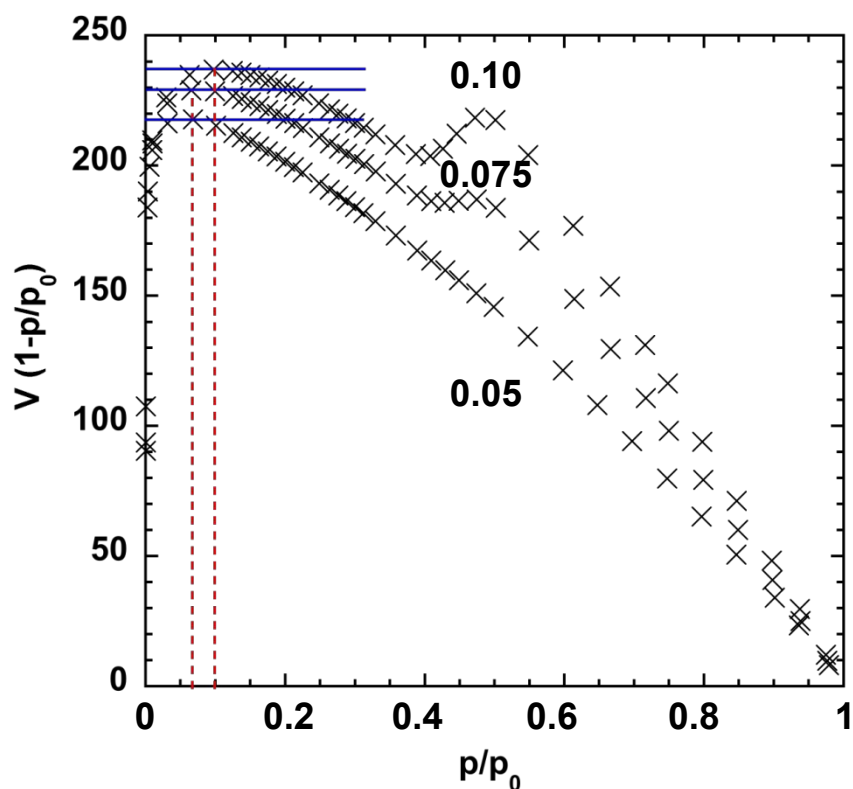


Figure 4. Examples of Rouquerol plots of hierarchical microporous/mesoporous FAUmes synthesized from H-FAU-Y with C18TAB surfactant and different NaOH/Si ratio (NaOH/Si = 0.05, 0.075, 0.10, indicated on each curves) to determine the highest p/p_0 pressure (corresponding to the crossing between red and blue lines) to use in the fit of the BET equation to calculate S_{BET} .

The total surface areas (S_{BET}) is constant (937 m^2/g) for FAU-Y and for untransformed FAU-Y ($0 < \text{NaOH/Si} < 0.05$), whereas S_{BET} increases from 894 to 956 m^2/g with increase of NaOH/Si ratio for $0.075 < \text{NaOH/Si} < 0.125$ and then remains constant (949 m^2/g) for higher values of NaOH/Si ($0.125 < \text{NaOH/Si} < 0.25$) (Table 1). The S_{BET} surface areas calculated from nitrogen adsorption isotherms are sensitive to the surface chemistry of the materials, as the cross-

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3 section of N₂ molecules can vary from 0.135 nm² for a hydrophilic surface to 0.162 nm² for a
4 hydrophobic surface depending on the orientation of the molecule with the surface.¹⁹ The latter
5 cross-section (0.162 nm²) is typically used in S_{BET} calculation (Eq. 3,4).
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10 In order to evaluate surface hydrophilicity, S_{BET} surface areas were also assessed from Ar
11 isotherms at 87 K. The S_{BET} calculated from the Ar isotherms were constant (780 m²/g) except
12 for untransformed FAU-Y materials (0 < NaOH/Si < 0.05), which show the highest surface areas
13 (820 m²/g). To analyze the micropore + mesopore surface areas of the materials, the external
14 surface areas (S_{ext})_{tpt} were subtracted from the total surface areas (S_{BET}) (Figure S6). The
15 resulting micropore + mesopore surface areas for FAUmes materials determined from Ar
16 isotherms were constant (740 m²/g) for all NaOH/Si ratio (0 < NaOH/Si < 0.25), whereas the
17 micropore + mesopore surface areas determined from nitrogen isotherms increase from 855 to
18 930 m²/g with increase in NaOH/Si ratio in the range 0 < NaOH/Si < 0.125 and then remain
19 constant (920 m²/g) for higher NaOH/Si ratio (0.125 < NaOH/Si < 0.25) (Figure S6).
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33 The Ar isotherm results show that the progressive increase of micropore + mesopore
34 surface area observed from N₂ isotherms for the 0.05 < NaOH/Si < 0.125 samples is due to a
35 change of the orientation of the nitrogen molecules on the surface. The progressive increase in
36 the hydrophilic character of the surface during the transformation into FAUmes arises from an
37 increase in the density of silanol groups on the surface of the materials.¹ FAU-Y and
38 untransformed FAU-Y (0 < NaOH/Si < 0.05) feature a hydrophobic surface as silanol groups are
39 isolated and nitrogen molecules are lying on the surface giving a cross-section of 0.162 nm². By
40 increasing the NaOH/Si ratio, silanol groups are formed¹ and the interactions between silanol
41 groups increase, increasing the hydrophilic character of the surface of FAUmes materials. N₂
42 molecules are progressively oriented more perpendicularly to the surface and N₂ molecules cross-
43 section decreases. The cross-section value of nitrogen molecules for the highest hydrophilic
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3 character of the materials (FAUmes synthesized with $0.125 < \text{NaOH/Si} < 0.25$) corresponding to
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5 920 m²/g instead of 855 m²/g can be estimated by assuming a constant BET surface area for all
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7 materials (as demonstrated by Ar adsorption). The N₂ molecule cross-section would become
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9 0.1404 nm² instead of 0.162 nm².

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12 Corrections of S_{BET} determined by nitrogen have been done with this new nitrogen cross-
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14 section for FAUmes synthesized with $0.075 < \text{NaOH/Si} < 0.25$ and called S_{BET}* (Table 1). The
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16 micropore, mesopore and micropore + mesopore surface areas have been calculated for all
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18 materials using either S_{BET} or S_{BET}* taking also into account corrections of S_{mes+ext} determined by
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20 t-plot method (S_{mes+ext})_{cor}. S_{BET} was used for materials synthesized with $0 < \text{NaOH/Si} < 0.0625$
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22 and S_{BET}* for $0.075 < \text{NaOH/Si} < 0.25$. The micropore surface areas have been calculated from
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24 the difference of total surface areas (S_{BET} or S_{BET}*) with (S_{mes+ext})_{cor} and named (S_{mic})_{cor} or
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26 (S_{mic}*)_{cor}, respectively (Table 1). The mesopore surface areas were calculated by subtracting
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28 (S_{ext})_{tpt} from (S_{mes+ext})_{cor} and named (S_{mes})_{cor} (Table 1). The micropore + mesopore surface
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30 areas have been calculated by difference of S_{BET} or S_{BET}* with external surface areas (S_{ext})_{tpt}
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32 (Figure 5).
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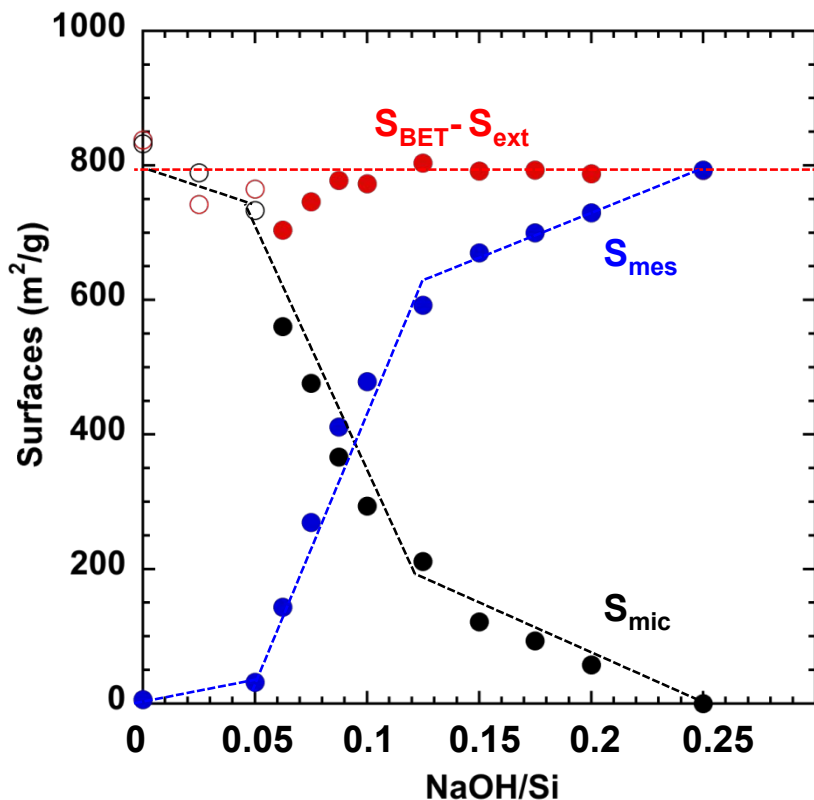


Figure 5. Micropore (S_{mic})_{cor} and mesopore (S_{mes})_{cor} surface areas of hierarchical microporous/mesoporous FAU-Y (FAUmes) synthesized from H-FAU-Y with C18TAB surfactant and different NaOH/Si ratio determined by t-plot analysis and corrections (Eq. 10-12). The micropore + mesopore surface areas of FAUmes ($S_{BET}-S_{ext}$) has been determined by subtracted the external surface (S_{ext})_{tpt} from S_{BET} or S_{BET}^* . S_{BET} or S_{BET}^* was calculated with nitrogen cross-section of 0.162 or 0.1404 nm² for FAUmes synthesized with NaOH/Si = 0 – 0.0625 and 0.075 - 0.25, respectively.

Surface area calculations for FAUmes materials show that the micropore surface areas (S_{mic})_{cor} decreases and the mesopore surface areas (S_{mes})_{cor} increases with the increase of the

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3 NaOH/Si ratio in the synthesis, while the micropore +mesopore surface areas remain constant
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5 (Figure 5). The transformation of FAU-Y into mesoporous FAU-Y occurs with the same surface
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7 area (micropore + mesopore surface areas) as FAU-Y (937 m²/g). The microporous surface is
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9 replaced by a mesoporous structure of similar surface area (954 m²/g for FAUmes synthesized
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11 with NaOH/Si = 0.25 with almost no microporosity). The transformation of FAU-Y into
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13 FAUmes is accompanied by an increase of the surface hydrophilicity. A FAUmes material
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15 featuring an equivalent micropore and mesopore surface area should be obtained with NaOH/Si =
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17 0.095 in the synthesis (Figure 5) and would feature an intermediate hydrophobicity/hydrophilicity
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19 in between FAU-Y and amorphous ordered mesoporous material as the one synthesized with
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21 NaOH/Si = 0.25 (Figure S6).
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28 CONCLUSIONS

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33 A methodology to decouple total, external, mesopore and micropore surface areas for micro-
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35 /mesoporous materials using the t-plot method and BET equation has been provided. S_{BET} can be
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37 used to evaluate the total surface areas (microporous + mesoporous + external surface) of micro-
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39 /mesoporous materials if the Rouquerol criterion is well respected. By using mechanical mixtures
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41 of FAU-Y and MCM-41 materials of experimentally determined micropore and mesopore surface
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43 areas, respectively, it was shown that mesoporous + external surface areas (S_{mes+ext}) determined
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45 by the t-plot are overestimated for materials containing more than 30% of micropore volume.
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47 Corrections for the overestimation of S_{mes+ext} have been provided. This methodology has been
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49 applied to decouple the micropore and the mesopore surface areas of a family of hierarchical
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51 micro-/mesoporous FAU-Y (FAUmes) synthesized from FAU-Y in presence of
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3 octadecyltrimethyl ammonium bromide and different NaOH/Si ratios ($0 < \text{NaOH/Si} < 0.25$).
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5 These characterizations of FAUmes show that the micropore surface area decreases and the
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7 mesopore surface area increases with the increase of NaOH/Si ratio, while the micropore +
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9 mesopore surface area remains constant. An equivalent micropore surface area and mesopore
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11 surface area is expected for a FAUmes material synthesized with $\text{NaOH/Si} = 0.095$. Comparisons
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13 of BET surface areas of FAUmes materials determined by N_2 isotherms at 77 K and Ar isotherms
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15 at 87 K show that FAU-Y features a hydrophobic character and that by transforming FAU-Y into
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17 FAUmes the hydrophilicity of the surface increases with the increase of NaOH/Si, especially in
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19 between $0.065 < \text{NaOH/Si} < 0.11$, and then the surface remains hydrophilic for $0.125 < \text{NaOH/Si}$
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21 < 0.25 . The combination of t-plot method and BET equation is a powerful tool to evaluate
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23 independently the micropore and mesopore surface areas of micro-/mesoporous materials.
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25 Equations given in this study to correct the overestimation of mesopore surface areas determined
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27 by t-plot method for hierarchical microporous/mesoporous materials apply to nitrogen isotherms
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29 at 77 K. However, these are not suitable for Ar adsorption at 87 K. Similar work will be
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31 performed to assess the micropore and mesopore surface areas from Ar isotherms in a future
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33 work.
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42 **ACKNOWLEDGMENTS**

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48
49 Goupil for discussions on t-plot standard isotherms comparison, M. Thommes for Ar adsorption
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51 isotherms at 87 K measurements and J. Rodriguez for low pressure nitrogen isotherms at 77 K.
52
53 We thank Professor Thomas J. Pinnavaia for help in editing the text to improve English grammar.
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55
56 A. Galarneau would like to dedicate this article to Pr. Kenneth Sing and Pr. Françoise Rouquerol,
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2
3 two important researchers in fundamental adsorption and the characterization of porous solids,
4
5 who passed away recently (2016 and 2017, respectively).
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10 **Supporting informations:** Additional t-plots of mechanical mixture of FAU-Y and MCM-41
11 and of mesoporous FAU-y (FAUmes). Additional Rouquerol plots. Comparison of mesopore +
12 external surface areas of the mechanical mixtures of FAU-Y and MCM-41 as a function of
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14 micropore surface area. Equations for the relationship between thickness t and p/p_0 for the
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16 analysis of the low pressure part ($p/p_0 < 0.01$) of the isotherms.
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Table 1. Textural features of hierarchical mesoporous FAU-Y (FAUmes) synthesized with C18TAB surfactant and different NaOH/Si ratios produced from nitrogen sorption isotherms at 77 K. Total, mesopore and micropore volumes and surface areas have been calculated using BET equation and t-plot analysis (tpt) and corrected values of t-plot (cor). For t-plot analysis Aerosil 200 was used as reference isotherm.

| NaOH/Si | S _{BET} | S _{BET} * | V _{tot} | V _{mic} | S _{mes+ext} | V _{mic} | V _{mes} | S _{mes+ext} | S _{mes} | S _{mic} | S _{mic} * | S _{ext} |
|---------|-------------------|--------------------|------------------|------------------|----------------------|------------------|------------------|----------------------|-------------------|-------------------|--------------------|-------------------|
| | | | tpt | tpt | tpt | cor | cor | cor | cor | cor | cor | tpt |
| | m ² /g | m ² /g | mL/g | mL/g | m ² /g | mL/g | mL/g | m ² /g | m ² /g | m ² /g | m ² /g | m ² /g |
| 0 | 937 | | 0.431 | 0.265 | 276 | 0.371 | 0.060 | 105 | 6 | 832 | | 99 |
| 0.025 | 868 | | 0.383 | 0.258 | 208 | 0.361 | 0.022 | 79 | -47 | 789 | | 126 |
| 0.05 | 861 | | 0.437 | 0.233 | 278 | 0.326 | 0.111 | 128 | 32 | 733 | | 96 |
| 0.0625 | 885 | | 0.479 | 0.222 | 339 | 0.311 | 0.168 | 206 | 143 | 679 | | 63 |
| 0.075 | 894 | 775 | 0.534 | 0.209 | 391 | 0.280 | 0.254 | 298 | 269 | 596 | 476 | 29 |
| 0.0875 | 923 | 780 | 0.592 | 0.190 | 474 | 0.242 | 0.350 | 433 | 411 | 490 | 366 | 22 |
| 0.10 | 926 | 802 | 0.634 | 0.180 | 509 | 0.222 | 0.411 | 509 | 479 | 417 | 293 | 30 |
| 0.125 | 957 | 829 | 0.714 | 0.149 | 618 | 0.170 | 0.544 | 618 | 592 | 339 | 211 | 26 |
| 0.15 | 949 | 822 | 0.766 | 0.116 | 701 | 0.122 | 0.644 | 701 | 670 | 248 | 121 | 31 |
| 0.175 | 960 | 832 | 0.782 | 0.102 | 739 | 0.103 | 0.678 | 739 | 700 | 221 | 93 | 39 |
| 0.20 | 956 | 828 | 0.790 | 0.085 | 771 | 0.085 | 0.705 | 771 | 730 | 185 | 58 | 41 |
| 0.25 | 954 | 827 | 0.811 | 0.057 | 827 | 0.057 | 0.754 | 827 | 793 | 127 | 0 | 34 |

*with S_{BET} calculated with nitrogen surface 0.1404 nm² for 0.075 < NaOH < 0.25

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3 **Graphical Abstract**
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12 Overestimation of
13 Mesopore Surface
14 by t-plots of micro/
15 mesoporous
16 materials

17 *Corrections provided

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19
20 $S_{mic} = S_{BET} - S_{mes+ext}^*$

21 $S_{mes} = S_{mes+ext}^* - S_{ext}$
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