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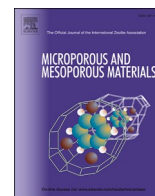
The Brunauer–Emmett–Teller model on alumino-silicate mesoporous materials. How far is it from the true surface area?

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ABSTRACT

Determining the surface area of porous materials through the Brunauer–Emmett–Teller (BET) model is a common practice. The method is generally applied in commercial software packages, where the assumptions are sometimes accepted by the experimenter whilst they may sometimes require a deeper analysis. One element of debate is the molecular cross-sectional area of the adsorptive. There is not yet agreement about the correctness of the BET model using a certain value for cross-sectional area of N_2; the conventionally-used parameter seems to overestimate the surface areas. In this work, a preliminary study of a modified method is presented, which introduces an 'apparent' cross-sectional area for N_2, which is smaller to the typically-used value. This value was obtained after measuring a number of relevant mesoporous materials in N_2 and Ar, using a model that considers an apparent value for the cross-sectional area. The model predicts outcomes very close to the Ar-based measurements in terms of low relative error. Then, we went one step further and looked into the geometrical surface areas, also referred to as true surface areas. By combining prior studies with our work, it was found that the surface area, using N_2 and the conventionally-used cross section, can be *ca.* 50% higher than the geometrical surface area. Therefore, the significance of the BET surface area seems to be far from well understood, though it is widely applied. This approach also allowed to define an 'effective' cross section for N_2, that relates it to the geometrical surface area. Its value agrees with prior considerations for an epitaxial orientation of the N_2 molecule with a hydroxylated silica surface. As a final recommendation, critical thinking is needed about the default settings in standardised calculations, which may not represent a reliable measure of the true surface area.

1. Introduction

Physical characterisation of solid materials has progressed notably in understanding the materials' properties, such as X-ray diffraction, small-angle X-ray and neutron scattering, mercury porosimetry, gas adsorption, NMR methods, electron microscopy, to cite a few. Gas adsorption is a commonly-used instrumental technique to characterise micro- and mesoporous materials [1–4], which covers a wide spectrum of pore sizes. In the last decades, significant progress has been made in gas adsorption [5–8]. Therefore, there is a better understanding about the true potential of gas adsorption and its limitations [9]. In the case of heterogeneous catalysts, the solid's porosity plays an important role in the catalyst performance. It is common practice to discuss activity-texture correlations where the BET model (Brunauer, Emmett and Teller) [10] is employed. BET measurements often rely on using N_2 as adsorbate because liquid N_2 is more accessible than Ar. However, using Ar brings more realistic values due to reasons explained below.

Using N_2 in the BET model is generally employed but this approach has some limitations. The BET method consists of two steps. In the first one, the physisorption isotherm needs to be transformed in a BET plot, where the monolayer capacity is obtained. In the second step, the surface area is calculated. Such a calculation uses the experimentally-determined monolayer capacity in combination with the theoretical cross-sectional area of N_2 [2,3] through Equation (1):

$$S_{BET}^{N_2} = n_m^{N_2} \cdot \sigma_m^{N_2} \cdot N \tag{1}$$

Where $S_{BET}^{N_2}$ is the BET surface area, $n_m^{N_2}$ is the monolayer capacity (*i.e.* number of moles of N_2 in the completed monolayer), $\sigma_m^{N_2}$ is the cross-sectional area of N_2 molecule and N is the Avogadro's number. The typically-used value for the cross-sectional area of N_2, normally set in the commercial software by default, is an average value of 0.162 nm²/molecule. Such a quantity was derived by Emmett and Brunauer [11] assuming the N_2 molecule to be spherical in a close-packed liquid state at the adsorption temperature; calculations with the most recent measurement of the liquid density for N_2 show very good agreement with the original value [12]. However, there is vast evidence that in reality the cross-sectional area for N_2 depends on the surface chemistry and confinement effects, which some authors refer it to a dependency of the cross-sectional area with the *C* parameter of the BET model [13]. Accordingly, $\sigma = f\ (C)$ where $C = k \cdot exp\{\Delta E/RT\}$, ΔE being the neat molar heat of adsorption and *k* is a constant. Some authors consider a dependency of σ with the adsorbate-adsorbate interactions as well [14]; a situation that would be impossible to implement in the BET model since it ignores the influence of lateral adsorbate interactions. This study attempts to provide a way to improve the nitrogen BET surface area determination, for mesoporous alumino-silicate materials, using argon data as a point of comparison. The approach is based on the determination of 'apparent' nitrogen cross-sectional area by means of a comparison between nitrogen and argon physisorption data. Furthermore, preliminary insights about the relation between the geometric and N_2-derived BET surface areas are provided, using an 'effective' nitrogen cross-sectional area.

2. Experimental methods

2.1. Materials

The materials employed in this study are mesoporous silica and alumino-silicates. A description can be found in Table 1. Some are commercial and others were prepared in the lab. The following chemicals were employed to synthesize the SBA-15 materials: Tetraethoxysilane (TEOS, 98%, Aldrich), poly (ethyleneoxide)20-poly (propyleneoxide)70-poly-(ethyleneoxide)20 (Pluronic®-P123, Sigma-Aldrich) and hydrochloric acid (HCl, 37 *wt* %, ACROS).

2.2. Synthesis of the SBA-15

The SBA-15 materials were synthesized according to the method reported elsewhere [15,16]. In a synthesis, the following compounds were mixed to obtain a homogenous mixture: 8 g of P123 were mixed with 240 g HCl (2.0 M) and 60 g of Mili-Q water. The mixture was mildly heated at 313 K. After that, *ca.* 17 g of TEOS were added drop-by-drop in ca. 25 min. The gel has a molar composition of SiO_2:0.017 P123:5.9 HCl:$204H_2O$. The synthesis was ended after 20 h at 313 K to complete the hydrolysis. The slurry was hydrothermally treated at two distinct temperatures; 383 and 403 K for 24 h. The slurry was then filtered and the so-obtained solid was washed with abundant deionized water (ca. 2 L per batch). The materials were dried overnight at 358 K. The corresponding SBA-15 materials are denoted as SX where X represents the aging temperature. The calcination was carried out by heating the sample in static air at a rate of 1 K/min until 823 K or 1173 K and kept 6 h, in a Nabertherm box furnace model LT9/11 equipped with a P330 temperature controller. The suffix HT is added to the sample code when these were calcined at 1173 K, meaning high-temperature. The high-temperature treatment was done to reduce the surface area and expand the number of materials.

2.3. Characterization methods

Gas sorption measurements were obtained from an ASAP2020 adsorption analyzer (Micromeritcs) by using N_2 at 77 K (liquid N_2 temperature) and Ar at 87 K (liquid Ar temperature). The samples were degassed at 623 K for 4 h. The Brunauer-Emmet-Teller (BET) method was applied for total surface area evaluation and the pore size distribution was analysed by the BJH model. Small angle X-ray scattering (SAXS) patterns were obtained from a NanoStar instrument (Bruker), containing a ceramic fine-focus X-ray tube powered with a Kristallflex K760 generator (35 kV, 40 mA). The primary X-ray beam was collimated in cross-coupled Gobel mirrors and a pinhole of 0.1 mm in diameter, resulting in a CuKα radiation beam with a full width at half maximum of *ca.* 0.2 mm. The sample-to-detector distance was 104 cm. The scattering X-ray was recorded with a Siemens AXS Hi-Star position-sensitive area detector in the range of 0.1–2.0 nm. The SAXS spectra were integrated with the mathematical Chi method.

3. Results and discussion

3.1. Apparent cross section for nitrogen using argon-validated measurements

When using nitrogen as probe molecule in physical adsorption, one has to consider that it has a quadrupolar moment. It is therefore expected that the cross-sectional area changes with the polarity of the surface (*e.g.* with the hydroxyl density for oxides) and the confinement imposed by the pores. The idea of the surface chemistry is illustrated in

Table 1
Description of the materials, experimental and derived textural parameters.

Material	Description	Φ (nm)[b]	Ordering[c]	Data obtained from N_2 at 77 K			Data obtained from Ar at 87 K		
				V_m[d]	S_{BET}[e,g]	C	V_m[d]	S_{BET}[f,g]	C
				(cm³/g STP)	(m²/g)	(−)	(cm³/g STP)	(m²/g)	(−)
GA	γ-alumina, Albemarle	11.0	D	62.5	272.0	101	59.6	227.4	36
NP55	Silica-Alumina, Saint Gobain NorPro, SS61155	7.2	D	91.9	400.0	108	87.1	332.2	27
NP38	Silica, Saint Gobain NorPro, SS61138	19.7	D	52.7	229.5	94	48.1	183.7	27
G10	Silica, Fuji Silysia, G-10	24.5	D	65.1	283.6	129	58.8	224.4	24
S383	All silica SBA-15 (383/823),[a] self-prepared	7.6	S	183.1	797.0	118	169.0	644.8	33
S403	All silica SBA-15 (403/823),[a] self-prepared	10.0	S	144.5	629.2	115	133.5	509.5	33
S383.HT	All silica SBA-15 (383/1173),[a] self-prepared	7.6	S	109.1	475.1	84	102.3	390.5	31
S403.HT	All silica SBA-15 (403/1173),[a] self-prepared	9.2	S	107.5	467.8	80	99.0	377.8	30

[a] Values in parenthesis corresponds to ageing temperature/calcination temperature, in K.
[b] Average pore size determined from Ar at 87 K as $4 \times 10^3\ V/S_{BET}$, where *V* is the total pore volume determined at *P/Po* ~0.97 in the desorption branch.
[c] S = structured material, D = disordered material.
[d] Monolayer capacity determined experimentally.
[e] Using 0.162 nm²/molecule for N_2.
[f] Using 0.142 nm²/atom for Ar.
[g] The significance of the decimals in the BET values is only as a mathematical value to calculate the error. Often, the BET can be reported as an integer.
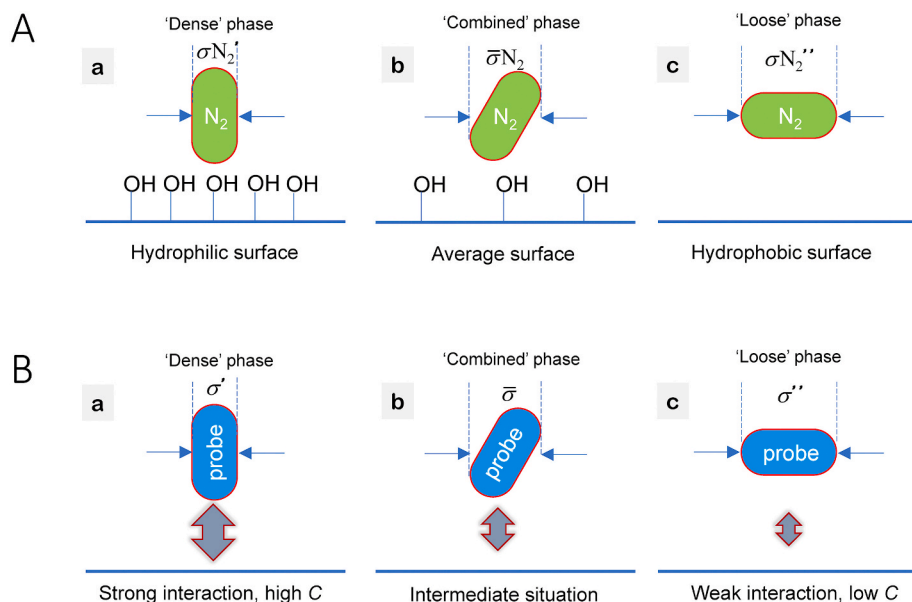
Fig. 1. A) Oxide materials. Models representing the various manners a N_2 molecule can interact with a hydroxylated solid surface depending on the polarity for a hydrophilic (**a**), average (**b**) and hydrophobic surface (**c**). Cases **a** and **c** have been exaggerated to highlight the concept. **B)** More general interpretation based on the interaction between adsorbent's surface and the probe molecule: strong (**a**, high C in the BET model), weak (**c**, low C in the BET model) and (**b**) an intermediate situation. Note that confinement effects can influence as well the C value in addition to the surface chemistry.

Fig. 1A with a hydroxylated surface, where the N_2 cross sectional area is narrow for a highly-hydroxylated surface (Fig. 1A–a), while it would be wider for a hydrophobic surface (Fig. 1A–c). The typically-used value in BET calculations, 0.162 nm^2/molecule, would correspond to an intermediate situation, as indicated in Fig. 1A–b. The consequence of this approach is that the BET surface area using such average cross-sectional area of 0.162 nm^2/molecule, results into an overestimation for more hydrophilic surfaces; as the true cross-sectional area should be smaller than the average value; the opposite is expected for hydrophobic surfaces. A more general interpretation is given in Fig. 1B, based on the interaction between adsorbent's surface and the probe molecule: strong (high C in the BET model), weak (low C in the BET model) and an intermediate situation; noting that the confinement effects can also influence the C value in addition to the surface chemistry.

In a study about the BET model, Jelinek and Kovats [17] proposed various values of the cross-sectional surface depending on the surface polarity, for the estimation of the true surface area with N_2. The values ranged from 0.135 up to 0.177 nm^2/molecule. For hydrated silica, the proposed value was 0.135 nm^2/molecule. Such a study was carried out on non-porous well-defined spherical particles with geometrical areas below 6 m^2/g. We wonder if such a value, or approximation, would be applicable to mesoporous materials, structured and disordered, of much larger surface areas. In other words, we investigated materials with more relevance from the application point of view for adsorption and catalysis.

A more accurate adsorbate for BET determinations would be argon. Due to the absence of molecular quadrupole moment, argon has a more spherical shape and the cross-sectional area is less sensitive to the adsorbent's surface polarity. Because of the lack of specific interaction between Ar and the pore walls (or much less than N_2), the pore filling dependency with the size is more straightforward than N_2 [9]. The cross-sectional area for Ar has been considered less sensitive to the surface polarity with a customary value of 0.142 nm^2/molecule at 87.3 K [9,18] (a range of other values have been reported; see dataset by McClellan and Harnsberger [19]). Note that Ar may be polarised, but it is expected to be less sensitive than N_2 in terms of the cross-sectional area upon polarisation. Argon can be considered a good first approximation to the true (geometric) surface area.

Although the effect of the OH density has been employed in Fig. 1A to illustrate the problematic, such a parameter (OH/nm^2) was not included in the model because besides the surface chemistry, the confinement effects should be considered. Later on, it will be seen that

the C parameter, for the studied mesoporous materials, oscillates using both N_2 and Ar. If the surface chemistry would be the only parameter, the C values for the Ar measurements should remain more constant, but it is not (Table 1). This is an indirect evidence that confinement also plays a role. Moreover, the OH density should be defined per true (*i.e.* geometric) surface areas, and those values are unknown. To tackle this problem rigorously, the model should include C as a key parameter that would comprise the surface chemistry and confinement. Because of the above complexity, a different approach was employed as discussed below.

As a practical example of catalyst preparation of supported species [20], it is often required to know the accurate value of the geometric surface area, or close to this, in order to prepare catalysts with a certain monolayer loading of active species (*e.g.* metals). But more generally, knowing the true value of the surface area is crucial to correlate the catalytic, or adsorption, phenomena to the catalyst properties. Argon measurements would give a closer value to the geometric surface area. In the case that liquid Ar is unavailable in the lab, and is also a more expensive chemical than liquid N_2, the question is whether improved BET values can be determined using N_2 as adsorptive (liquid N_2 is widely available in analytical labs). Therefore, the question can be mathematically stated as follows; whether an 'apparent' cross-sectional area can be obtained that would render similar BET values as those obtained with Ar, Equation (2):

$$S_{BET}^{Ar} = n_m^{Ar} \cdot \sigma_m^{Ar} \cdot N = n_m^{N_2} \cdot \overline{\sigma_m^{N_2\ app}} \cdot N \tag{2}$$

where S_{BET}^{Ar} is the Ar-based BET surface area, n_m^{Ar} is the Ar-based monolayer capacity, σ_m^{Ar} is the cross-sectional area of Ar and $\overline{\sigma_m^{N_2\ app}}$ is an average 'apparent' cross-sectional area for N_2 that would enable using experimental data from N_2 measurements. If Equation (2) holds true, then the apparent cross-sectional area for N_2 can be obtained from Equation (3), after measuring a number of materials with N_2 and Ar, at the corresponding boiling liquid temperatures:

$$\overline{\sigma_m^{N_2\ app}} = \sigma_m^{Ar} \cdot \left(\frac{n_m^{Ar}}{n_m^{N_2}} \right) = \sigma_m^{Ar} \cdot \left(\frac{V_m^{Ar}}{V_m^{N_2}} \right) \tag{3}$$

The objective of this study is to investigate if such a method is feasible. For this, we analysed a number of mesoporous alumino-silicate materials which were subjected to N_2 and Ar measurements, and the above model was applied for its validity. We made sure that the

materials only contain mesoporosity; having microporosity can lead to an undesired overestimation of the monolayer capacity (see comment about SBA-15, below).

It is well known that the BET values on silicas depend on the range of the relative pressure employed in the calculations [21,22], therefore,

care was given in choosing the same interval of the relative pressure to derive the BET values and exclude such an uncontrolled variable. The materials employed in this study are mesoporous silica and alumino-silicates, both structured and disordered, and they represent materials of possible industrial use. A description can be found in
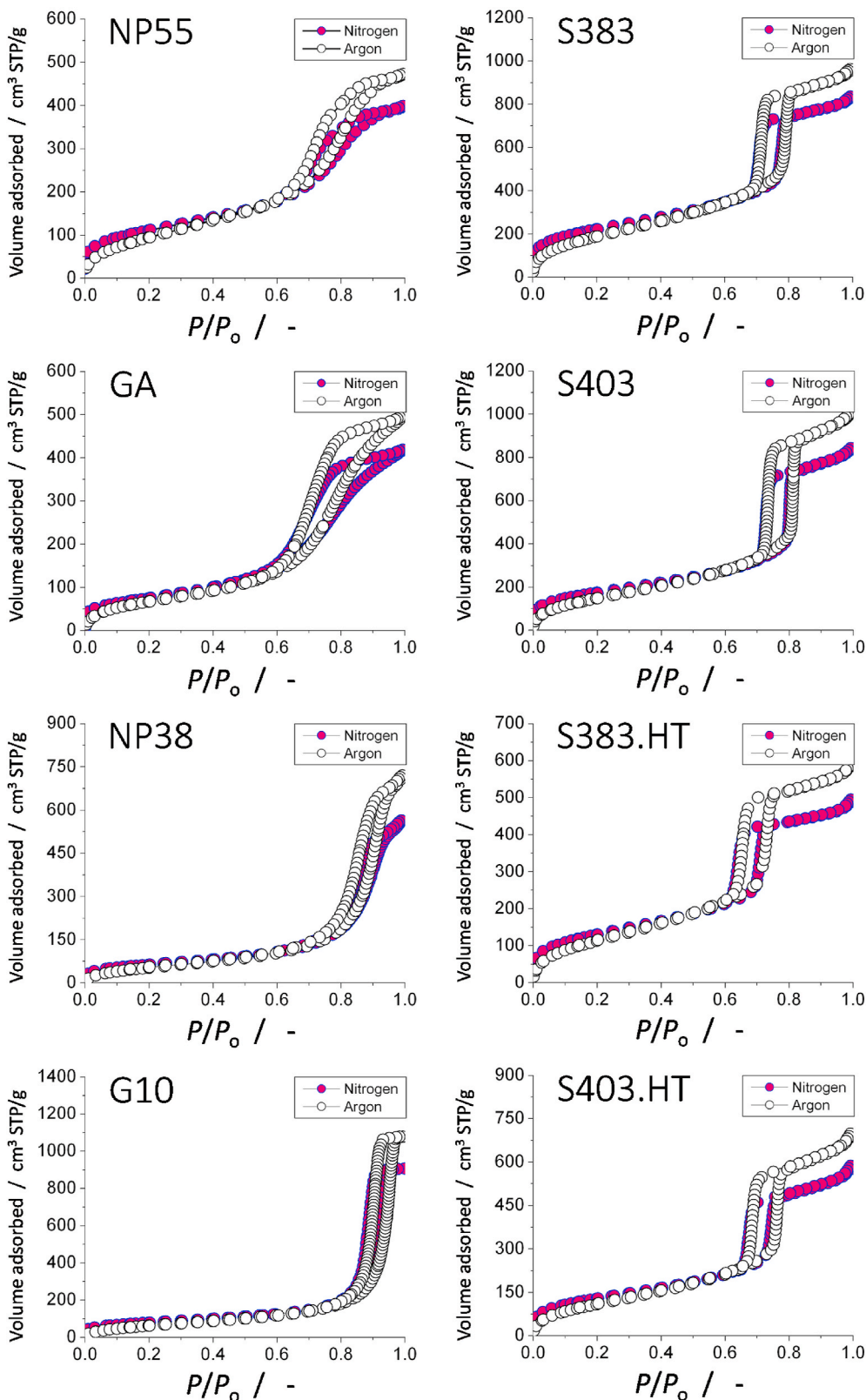

Fig. 2. Physisorption isotherms for the studied materials, N_2 at 77 K and Ar at 87 K.

Table 1. Some are commercial products and others (SBA-15 types) were prepared by us. The average pore size ranged from ~7 up to ~25 nm. In the case of the SBA-15 materials, it was verified that those do not contain any appreciable microporosity due to the applied hydrothermal temperatures in their synthesis, *i.e.* a sufficiently-high hydrothermal ageing removes the wall microporosity. Consequently, the SBA-15 materials are purely mesoporous. These materials were also subjected to a high-temperature (1173 K) treatment in order to reduce the surface area and therefore expand the range of the studied cases. Such a temperature did not alter the structure, and remained hexagonal as it can be seen in Fig. S1, in the Electronic Supporting Information. The BJH pore size distributions (Fig. S2, Electronic Supporting Information) show that the pore is reduced upon the thermal treatment for both materials. If the pore size would have been increased, then the lower surface area would be due to larger pores. However, in the case that the pore diameters are smaller, the reduced surface area can be assigned to densification, *i.e.* the highly-treated materials contain more mass per unit volume. This was rationalised by Zarubina and Melián-Cabrera [23] for another mesoporous silica upon thermal treatment at similar temperatures. Note that the reduction in the pore size for the SBA-15 upon thermal treatment is less sensitive using the average pore size concept, because this employs the total pore volume.

The solids, in a fine powder form, were analysed by gas adsorption using N_2 and Ar at their corresponding boiling liquid temperatures. Fig. 2 shows all the isotherms in N_2 and Ar, whereas the BET plots are given in Fig. 3. For the latter, the applied range of P/P_o in the calculation

has been highlighted, which was equal in all the analyses. The isotherms in Fig. 2 are of type IV with hysteresis H1, representing solids with cylindrical pore geometry, though the pores can be tortuous, with a high pore size uniformity and facile pore connectivity. The mesopore capillary condensation takes place in all the cases at $P/P_o \geq 0.6$, that is far away from the BET linear plot range (P/P_o between 0.05 and 0.2, Fig. 3); therefore, there is no influence of the mesopore capillary filling on the monolayer capacities (nor from the microporosity since this is absent in the studied materials). A summary of the derived parameters is given in Table 1. In all cases, the *C* parameters of the BET model were positive and the regression coefficients (r^2) were above 0.999 (not shown). It was always found that the parameters obtained from Ar were smaller than those with N_2, which is in line with previous literature observations [21] that nitrogen overestimates the surface areas, as compared to Ar.

Table 1 compiles the monolayer capacities (as V_m) derived from the BET plots. These values were employed to estimate the apparent cross-sectional area using Equation (3). The values are plotted in Fig. 4 together with the average quantity which was 0.132 nm^2/molecule. The plot visually shows that there was no significant variability; the standard deviation was 0.002 nm^2/molecule, which corresponds to 1.7% with respect to the average value. Based on the good fit of these results, the surface areas of the same materials were calculated using such an average apparent cross-sectional area, $\overline{\sigma_m^{N_2\ app}}$. The results can be found in Fig. 5A that compares the surface area from N_2 using the conventionally-employed value (0.162 nm^2/molecule), Ar using the 0.142 nm^2/molecule and the model calculation with 0.132 nm^2/
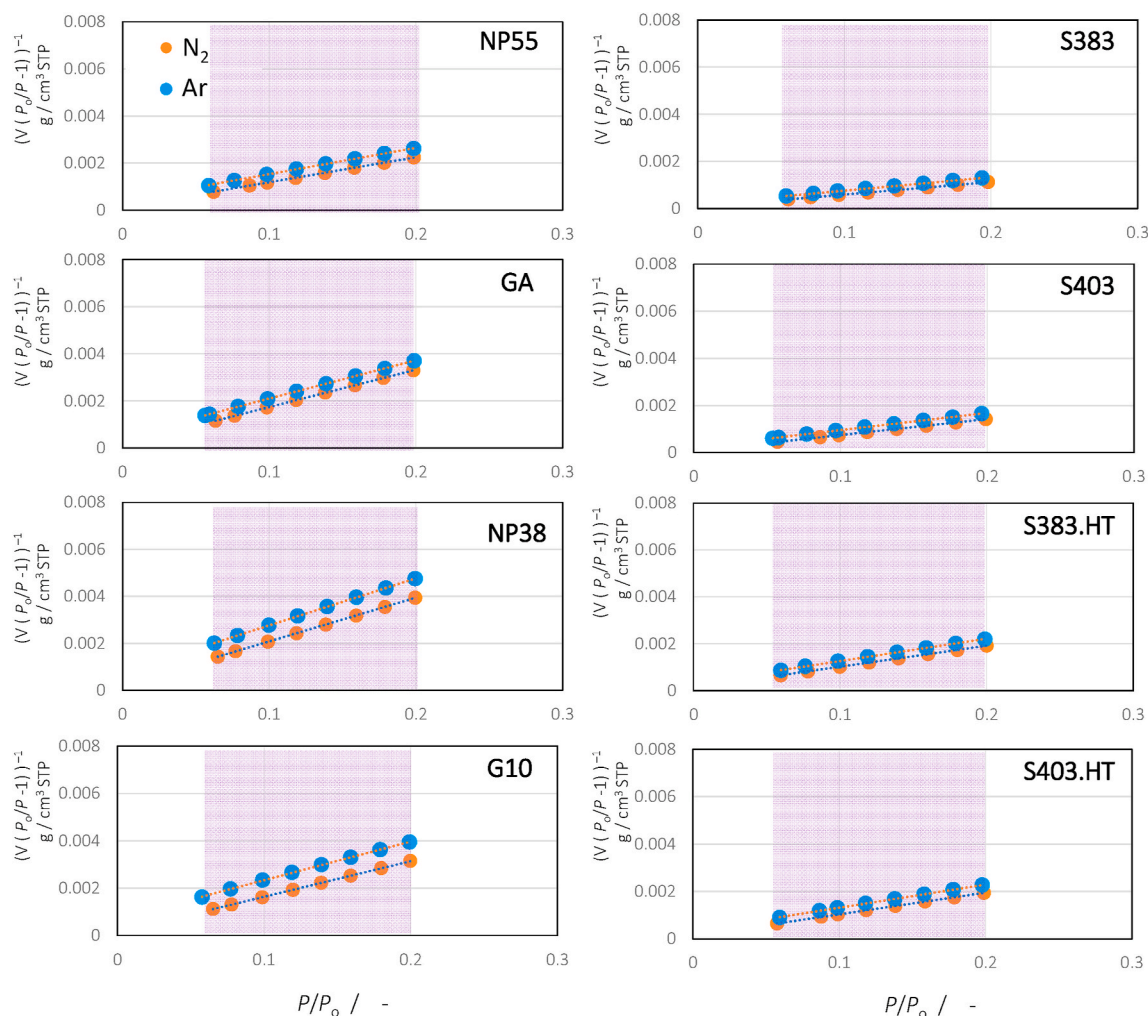

Fig. 3. BET plots for the studied materials under N_2 (77 K) and Ar (87 K).
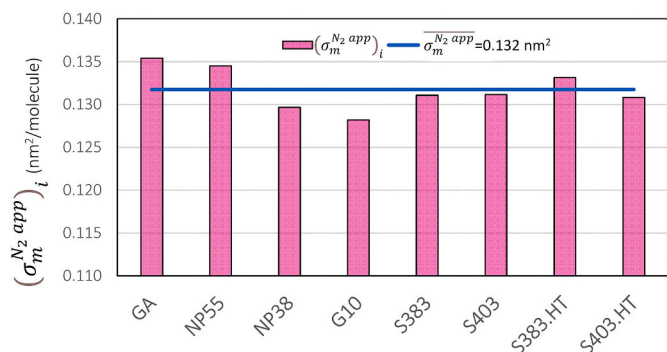
Fig. 4. Apparent cross-section for N_2 for various relevant mesoporous materials, including the average value as a horizontal line.
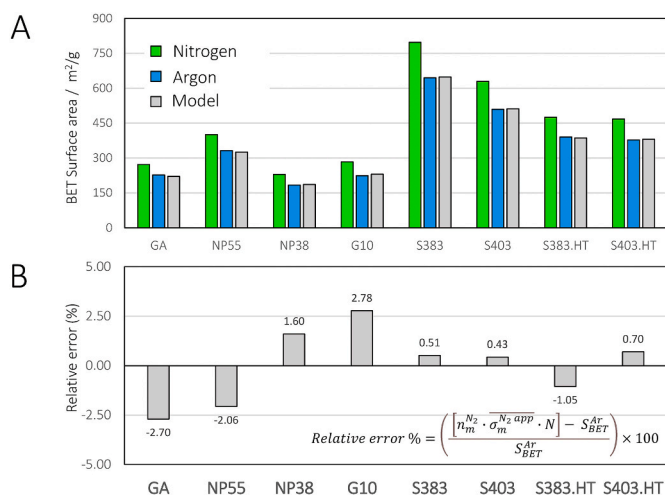

Fig. 5. A) Comparison of the surface areas determined from N_2, Ar and the proposed model; **B)** relative error in the surface areas determined from the proposed model. Raw data for the model calculation and relative error are given in Table S1 of the Electronic Supporting Information.

molecule. The model calculation nearly matches the values obtained with Ar. To highlight the good fitness of the results, Fig. 5B compares the error estimation using Equation (4) of the model with respect to argon; the relative error fluctuated between 0.4 up to 2.8%.

$$Relative\ error\ (\%) = \left(\frac{\left[n_m^{N_2} \cdot \overline{\sigma_m^{N_2\ app}} \cdot N \right] - S_{BET}^{Ar}}{S_{BET}^{Ar}} \right) \times 100 \qquad (4)$$

The higher difference between Ar and N_2 surface areas in Fig. 5A for the SBA-15 materials can be explained with this model. Equation (5) can be obtained using equations (1) and (2). It shows that the difference is proportional to the absolute value; since SBA-15 materials have higher BET values, the differences are higher.

$$\Delta\left(m^2/g\right) = S_{BET}^{N_2} - \left[S_{BET}^{Ar} \right]^{Model\ Eq.\ 2} = \left(1 - \frac{\overline{\sigma_m^{N_2\ app}}}{\sigma_m^{N_2}} \right) S_{BET}^{N_2} = 0.185 S_{BET}^{N_2} \qquad (5)$$

To put the results in context, we will compare these findings with prior work. The apparent cross-sectional value was very close to the one proposed by Jelinek and Kovats [17], comparing geometrical with N_2-derived data for nonporous materials. However, this work uses a different approach (comparing Ar with N_2-derived data) and we investigated materials with much higher surface areas and having intra-particle porosity. The typically-used parameter for BET calculations (0.162 nm^2/molecule) has been systematically used ever since the first reports on the BET model [10,11], though its correctness has been

criticized by some authors [1,17,24]. Despite that, the value is still widely used. It is important to note that when comparing BET values for similar mesoporous materials, in particular when looking at the relative changes in texture/porosity, such an assumption in the σ_m may be less relevant, since researchers are interested in the relative change. However, it brings concerns when comparing different types of materials, or when the absolute value of the true surface area (also often denoted as geometric surface area) needs to be known as accurately as possible. The results presented in this section proves that such an assumed value for σ_m gives an overestimation of the surface areas, using nitrogen as probe molecule. Such an overestimation is not due to the range of the employed P/P_o, as previously suggested [21], but to the cross-sectional area of the probe molecule (Note: it may happen that changing the P/P_o range produces differences between both probes, but this is a mathematical artifact. That is why it is recommended to fix the P/P_o range to avoid it). Therefore, although the BET surface area is a widely-accepted parameter, care should be given in the intrinsic calculation, and whether the end result represents a reliable value in your investigation.

3.2. A note about geometric surface areas

The next question is understanding how far we are from the true (geometric) surface area. For this, we can make use of previous work done on mesoporous materials. Coasne et al. [25] investigated the Ar adsorption on a model MCM-41 mesoporous material, and compared it with grand canonical Monte Carlo simulations. They found differences between the geometrical surface area and the one derived from the BET model of about 20% (Ar data), for cylindrical pores and a fully-hydroxylated surface. Their results were highly dependent on the C parameter (*i.e.* factors such as surface chemistry and confinement) and geometry of the pore. Considering their results and our data, it can be proposed the following relations between the geometric and the various BET surface areas.

Equation (6) can be derived from our results, combining Equations (1) and (2). It indicates that the conventional BET calculation produces surface areas ~23% higher than Ar data, Eq. (7):

$$S_{BET}^{Ar} = \left(\frac{\overline{\sigma_m^{N_2\ app}}}{\sigma_m^{N_2}} \right) S_{BET}^{N_2} = 0.815 S_{BET}^{N_2} \qquad (6)$$

$$\Delta(\%) = \frac{S_{BET}^{N_2} - S_{BET}^{Ar}}{S_{BET}^{Ar}} \times 100 = \frac{S_{BET}^{N_2} - 0.815 S_{BET}^{N_2}}{0.815 S_{BET}^{N_2}} \times 100 \approx 23\% \qquad (7)$$

Equation (8) was obtained from Coasne et al. [25] considering cylindrical pores and materials with the highest C value (ca. 22), since that value is the most compatible with our materials, which display C values ranging 24–36 (Argon measurements, Table 1):

$$S^{GEO} = 0.833 S_{BET}^{Ar} \qquad (8)$$

Equation (8) is based on cylindrical pores [25]. We think this can be a good approach for our materials since the pore size is larger than e.g. MCM-41; for the latter, the pore geometry would have a bigger influence on the surface area. However, this is an assumption we have made at this stage.

When combining Equations (8) and (6), it can be obtained that the conventionally-derived BET surface area can be *ca.* 47% higher than the geometric surface area, Equations (9) and (10):

$$S^{GEO} = 0.833 S_{BET}^{Ar} \times \left[\frac{\left(\frac{\overline{\sigma_m^{N_2\ app}}}{\sigma_m^{N_2}} \right) \times S_{BET}^{N_2}}{S_{BET}^{Ar}} \right] = 0.679 S_{BET}^{N_2} \qquad (9)$$

$$\Delta(\%) = \frac{S_{BET}^{N_2} - S^{GEO}}{S^{GEO}} \times 100 = \frac{S_{BET}^{N_2} - 0.679 S_{BET}^{N_2}}{0.679 S_{BET}^{N_2}} \times 100 \approx 47\% \qquad (10)$$

That means that N_2 is 23% higher with respect to Ar, whilst N_2 is 47% higher with respect to the geometric one, for this type of materials. It must be stressed that the values from Coasne et al. [25] are highly dependent on the surface chemistry and confinement. Therefore, it cannot be generally applied to any material. However, by taking a sensible value from their data set, we wanted to highlight that the N_2-derived BET surface areas can be far from the true surface areas, even though the methodology is widely applied and recommended by IUPAC [26].

Going one step forward, it is possible to connect the geometric surface area with the N_2-derived adsorption data, by defining a new cross-sectional area. It is termed as 'effective' to distinguish it from the 'apparent' in section 3.1. Such a parameter would relate the geometric surface area as follows:

$$S^{GEO} = n_m^{N_2} \cdot \overline{\sigma_m^{N_2\ eff}} \cdot N \qquad (11)$$

From Equation (1)

$$n_m^{N_2} = \frac{S_{BET}^{N_2}}{\sigma_m^{N_2} \cdot N} \qquad (12)$$

Introducing Eq. (12) in (11) results in:

$$S^{GEO} = \left(\frac{\overline{\sigma_m^{N_2\ eff}}}{\sigma_m^{N_2}} \right) S_{BET}^{N_2} \qquad (13)$$

or:

$$\overline{\sigma_m^{N_2\ eff}} = \sigma_m^{N_2} \left(\frac{S^{GEO}}{S_{BET}^{N_2}} \right) \qquad (14)$$

From Equation (9):

$$\frac{S^{GEO}}{S_{BET}^{N_2}} = 0.679 \qquad (15)$$

Introducing Eq. (15) in (14) results in:

$$\overline{\sigma_m^{N_2\ eff}} = 0.679 \sigma_m^{N_2} = 0.110\ nm^2 \big/ molecule \qquad (16)$$

This quantity is very similar to the one reported by Rouquerol et al. [14,27,28] for the case that the nitrogen molecules interact vertically with surface hydroxyl groups; the authors claimed that the N_2 cross-sectional value could be reduced to 0.112 nm^2 in the complete monolayer. However, the authors did not consider the relation of this parameter with the true surface area. The model proposed by Coasne et al. [25] in Equation (8) considers a fully hydroxylated surface. A situation that we have indicated in Fig. 1A–a, where the N_2 molecule would interact epitaxially with the surface, displaying a low value of the cross-sectional area, in agreement with Rouquerol et al. [14,27,28], and the obtained value from Equation (16).

The obtained value for $\overline{\sigma_m^{N_2\ eff}}$, that connects the geometrical with N_2-derived surface areas, is smaller than the one reported by Jelinek and Kovats for a silica-based material, 0.135 nm^2/molecule [17]. However, it must be kept in mind that the authors employed non-porous particles. It could well be that the here-obtained value includes the confinement effects since we analysed porous materials, as well as Coasne et al. [25]. We refer it to confinement by looking at the effect arising from the adsorption taking place within pores surrounded by walls; *i.e.* pores inside of a primary particle. Considering the overall data, it appears that the reduction from 0.162 to 0.135 nm^2/molecule [17] accounts for the OH surface chemistry, whilst the reduction from 0.162 to 0.110 nm^2/molecule ([25] and this work) accounts for surface chemistry and confinement (the geometry of the pore was not investigated here).

Our study brings a new understanding on the limitations of the BET model, with respect to the interaction of the probe with the surface. It is not a universal adsorption model but it is dependent on the adsorbent's surface structure. The study also suggests the need to develop more advanced models that enable to estimate the geometric surface areas. This should go in hand with the preparation of well-defined model mesoporous materials with a good estimation of the material dimensions; grain dimensions and pore size determined by high-resolution electron microscopy. With that information, a more universal model of the influence of C (*i.e.* surface chemistry and confinement) on the N_2-derived BET surface area may be established.

Fig. 6 provides an overview of the current understanding of the BET model, using prior studies [25] and this work. It was previously shown (α) that Ar gives an overestimation with respect to the geometric surface area (though the deviation was highly dependent on the C value and geometry). With the help of experimental isotherms in N_2 and Ar, of a range of mesoporous materials, a relationship between Ar- and N_2-derived surface areas was established where an 'apparent' cross-sectional area was defined (β). This study goes one step further and points towards a much higher deviation between the conventional N_2 data and the geometric surface area, with a worst-case deviation of about 50% (Eq. (10)). With conventional, it is referred to the widely-accepted cross section (0.162 nm^2/molecule). The proposed approach allows us to define an 'effective' cross-sectional area for N_2 that relates geometric with N_2-obtained surface areas (γ) of mesoporous alumino-silicate materials.

The authors became aware of a recently-reported work by Zou et al. [29], which was accepted after the submission of this work. They investigated the effect of the molecular cross-sectional area of adsorbed N_2 via the BET model for carbon-based slit pores, by means of grand canonical Monte Carlo simulations. They found that the cross-sectional area varies with the pressure, pore size and affinity between adsorbent/adsorbate. For pore sizes ranging 0.6–8 nm, the standard BET method using 0.162 nm^2/molecule causes an overestimation due to the cross-sectional area; adsorption in higher layers was also suggested to inflate the monolayer capacity and contributing to the deviation. The authors predicted smaller cross-sectional areas for cylindrical pores as the loading in cylindrical pores is denser, but those results are not yet reported. Their results are not directly comparable to ours, but they go in the same direction. It also agrees with our above-stated recommendation that more advanced models are required to bring the conventional BET values closer to the geometric surface areas.

4. Conclusions

This work describes a modified BET method to estimate Argon-validated surface areas, using nitrogen as probe molecule. For this, an 'apparent' cross-sectional area for N_2 was calculated from experimentally-determined measurements in N_2 and Ar, for a number of relevant alumino-silicate mesoporous materials, structured and disordered. The method gives very low relative errors and proposes a lower cross-sectional value for N_2, for such mesoporous materials. Though this is a preliminary study, it shows evidence that the way N_2 adsorbs is not universal, but it depends on the structure of the material's surface (*i.e.* surface chemistry and confinement) and that should be accounted for more accurate calculations. Preliminary insights were outlined about the relation between the geometric surface area and the values determined from the most conventional N_2 BET calculations. It shows that deviations of *ca.* 50% higher can be masking the significance, for a worst-case scenario using assumptions from prior studies. For this latter approach, we introduced an 'effective' cross-sectional area for N_2 which agreed with prior considerations for an epitaxial orientation of the N_2 molecule with a hydroxylated silica surface. More widely, we have also aimed to highlight that the physical meaning of what we call 'BET surface area' is far from well understood.

CRediT author statement

All authors contributed equally. The original idea was proposed by I. M.C. Financial acquisition was achieved by I.M.C. and L.L.P.
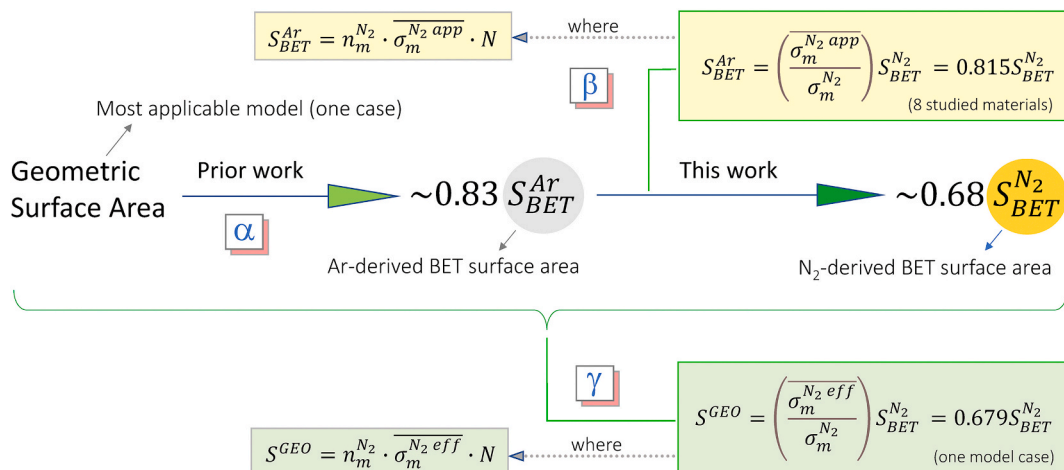
Fig. 6. Overview of the current understanding about the BET model on mesoporous alumino-silicate, considering prior art [25] (α) and the conclusions from this work. (β) This relationship relates the Ar-derived data with N_2 using an apparent cross-sectional area. (γ) Relationship between the geometric surface area with N_2-derived surface area for mesoporous alumino-silicate materials, considering the most applicable model from Ref. [25]. Equations (2), (6), (11) and (13) have been included for the sake of completeness.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2021.111065.

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