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FEATURES OF BET METHOD APPLICATION TO VARIOUS ADSORBENTS

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For various adsorbents, especially nanoporous, there is an applicability problem of the Brunauer−Emmett−Teller (BET) method using nitrogen as a probe adsorbate. Therefore, the nitrogen adsorption ($a(p/p_0)$) isotherms in several pressure ranges of the BET method at p/p_0 = 0.05–0.3, 0.06–0.22, and narrower are analyzed for a large set (about 200 samples) of essentially different adsorbents such as fumed oxides (individual, binary and ternary, initial and modified), porous silicas, activated carbons and porous polymers. Graphitized carbon black ENVI–Carb composed of nonporous nanoparticles aggregated into microparticles is used as a standard adsorbent characterized by the standard area occupied by nitrogen molecule $\sigma_m(N_2)$ = 0.162 nm². For initial nanooxides composed of nonporous nanoparticles, the standard value of σ_m = 0.162 nm² results in the overestimation of the S_{BET} values by ca. 10 % because of non-parallel-to-surface orientation of slightly polarized N_2 molecules interacting with polar surface functionalities (e.g., various hydroxyls). For nanooxides modified by low- and high-molecular (linear, 2D and 3D polymers and proteins) compounds, the overestimation of S_{BET} at σ_m = 0.162 nm² could reach 30 %, as well as for some activated carbons. For adsorbents possessing nanopores (at half-width x or radius R < 1 nm) and narrow mesopores (1 nm < R < 3 nm), an overlap of monolayer and multilayer sorption (giving apparent underestimation of S_{BET} at σ_m = 0.162 nm²) and non-parallel-to-surface orientation of the N_2 molecules (causing σ_m lower than 0.162 nm²) could lead to various location of the normalized nitrogen adsorption isotherms (in the BET range) with respect to that for ENVI–Carb. It could be characterized by positive or negative values of the BET constant c_{BET}. Two main criteria showing the inapplicability or applicability of the BET method (with nitrogen as a probe) related to the c_{BET} values and a course of reduced adsorption $a×(1−p/p_0)$ vs. p/p_0 in the BET range could not be in agreement for adsorbents, which are not pure nanoporous, but they are in agreement for pure nanoporous or meso/macroporous adsorbents.

Keywords: nitrogen adsorption isotherms, Brunauer−Emmett−Teller method restrictions, nanooxides, porous silicas, carbons, porous polymers

INTRODUCTION

The Brunauer–Emmett–Teller (BET) method [1] widely used to evaluate the specific surface area (SSA, S_{BET}) of various adsorbents is characterized by a certain weakness in the theoretical basis [2–7]. Under controlled conditions, the values of S_{BET} for nonporous (*e.g.*, highly disperse powders such as fumed oxides composed of nonporous nanoparticles, NPNP), macroporous or mesoporous adsorbents (with well–defined type II or type IV(a) isotherms [2, 3], respectively) could be considered as an accessible SSA for used probe adsorbate (*e.g.*, nitrogen, argon, benzene, *etc.*, as a whole, giving different S_{BET} values for the same adsorbent) [2–7]. The BET method application is of two simple stages. First, probe adsorption isotherm should be transformed (linearized) into the BET plot (within the corresponding pressure range, *e.g.*, p/p_0 = 0.05–0.3 or 0.6–0.22) to compute the values of monolayer adsorption capacity a_m and

BET constant c_{BET}, as a slope and Y–intercept, respectively, obtained using a linear approximation of the BET plot, which could demonstrate some deviation from the linear course. Second, the S_{BET} value is computed using the a_m value and an appropriate value of molecular cross–sectional area σ_m occupied by a sorbate molecule located in a complete monolayer: $S_{BET} = a_m N \sigma_m / M$, where N is the Avogadro number, and M is the molecular weight of adsorbate [1–7].

According to the BET theory [1–5], the parameter c_{BET} is exponentially linked to the free energy of monolayer sorption, and it gives useful information on an isotherm shape in the BET method range. If the c_{BET} value is, at least, ≥ 80, the isotherm knee is sharp and the related point B is well defined as the boundary between monolayer and multilayer adsorption. In other words, the characteristic point B, according to the BET theory [1–5], corresponds to a stage of

monolayer completion (*i.e.*, the end of the BET pressure range) and the beginning of multilayer sorption. If the c_{BET} value is low ($c_{BET} < 50$) that the point B cannot be well identified as a single point since there is an overlap of monolayer and multilayer sorption, and the accurate interpretation of a_m is rather questionable. If $c_{BET} < 2$ and the isotherm is of type III or V that the BET method is rather not applicable. A great value of c_{BET} (> 150) is associated with the adsorption on high–energy surface sites or with infilling of nanopores [2–7], and at very great c_{BET} values (> 450), the BET method application is rather questionable.

A convenient pathway to compute the value of a_m with the BET equation is based on a linear form. The range of BET plot linearity (or small deviation from the linear course) is restricted to a limited part of the isotherms, often $0.05 < p/p_0 < 0.3$ for type II and IV(a) isotherms. For type IV(b) isotherms, caution is required since probe condensation in pores (multilayer adsorption) could occur at quite low p/p_0 (*e.g.*, optimal $p/p_{0,max}$ could be lower as *ca.* 0.2 [8]). Typically, the linear BET range is shifted toward lower pressures if the sorption energy is high, especially for a surface energetically homogeneous or crystalline, *e.g.*, for nitrogen or argon sorption on graphitized porous carbon, or xenon sorption on porous metals [2–5]. As a whole, the S_{BET} values depend on (i) sorptive/sorbate structures, probe molecules orientation at a surface (*i.e.*, σ_m), temperature, and (ii) a procedure used to locate the pressure range appropriate to be used for the BET equation application. Nitrogen (boiling temperature 77.35 K) is a traditional sorptive used to calculate the S_{BET} values with standard $\sigma_m(N_2)$ assumed to be 0.162 nm^2 (based on the assumption of a closed–packed monolayer with molecules located parallel to a surface that is true for graphite-like surfaces but not true for many others, *e.g.*, oxide or polymeric adsorbents) [2–5, 9]. The wide use of nitrogen is due to the fact that liquid nitrogen is quite available, and because nitrogen isotherms for various sorbents exhibit a well–defined point B as the boundary between the monolayer and multilayer adsorption. However, the quadrupole moment of N_2 and certain polarization at a polar surface (*e.g.*, metal oxides) affect the orientation of nitrogen molecules depending on the sorbent surface chemistry [5, 8]. This could lead to uncertainty in the $\sigma_m(N_2)$ value up to 20 % or more

for some surfaces. Argon could be an alternative probe for SSA estimation since Ar molecules do not have a quadrupole moment and are less reactive than the diatomic nitrogen molecules. There are, however, several reasons why Ar is considered to be less reliable as a probe at 77.4 K than nitrogen [2–7]. At 77.4 K, argon is *ca.* 6.5 K below the bulk triple point temperature; therefore, the bulk reference state is in doubt. However, the Ar sorption could be used at 87.3 K, *i.e.*, at liquid argon temperature with no problems encountered with Ar at 77.4 K. At 87.3 K, a cross–sectional area, $\sigma_m(Ar)$ of 0.142 nm^2 is usually assumed. Because of the absence of a quadrupole moment and the higher temperature, the $\sigma_m(Ar)$ value is less sensitive to differences in the structure of a sorbent surface (*e.g.*, polar surface functionalities) affecting the $\sigma_m(N_2)$ value. The Ar sorption at 87.3 K offers some advantages for nano/mesopore analysis [2–7]. However, for Ar and N_2 at low temperatures (87.3 K, 77.4 K), there are certain kinetic restrictions. This suggest that both Ar and N_2 sorption is rather inappropriate for the characterization of very narrow nanopores. To solve this problem, the sorption of CO_2 (kinetic size of 0.33 nm) could be used at 273 K [4–7]. However, the nitrogen adsorption remains most popular for the textural characterization of various adsorbents. Therefore, the present study is focused on the BET method based on the N_2 adsorption for various adsorbents.

The BET method could be well applied to type II and IV isotherms, but a caution is needed if nanopores are present (with type I isotherms and combinations of types I and II or types I and IV isotherms) [2–7]. In this case, it could be difficult or even impossible to separate the processes of monolayer and multilayer sorption and nanopore infilling. For nanoporous sorbents, the linear range of the BET plot could be difficult to locate. However, there is a useful procedure allowing one to overcome this difficulty and avoid any subjectivity in evaluating the BET monolayer capacity. This procedure is based on the following main criteria: (i) the c_{BET} value should be positive (*i.e.*, a negative intercept on the ordinate of the BET plot is an indication that it is out of an appropriate range); (ii) application of the BET equation should be restricted to the range with $a \times (1 - p/p_0)$ continuously growing with p/p_0; and (iii) the p/p_0 value corresponding to a_m should be within the BET range [2–7]. Note that this procedure could not be expected to confirm the

validity of the BET monolayer capacity. Thus, the BET area derived from a type I isotherm should not be treated as a realistic probe accessible SSA. Instead of the nitrogen adsorption, the sorption of benzene and carbon dioxide (at room temperature) could be used to estimate the textural characteristics of sorbents. However, the use of these probes has both advantages and disadvantages [2–7].

$$ S_\varphi = \int\limits_{a_{\min}}^{a_{\max}} \frac{3}{2a^3\rho} \left[2(a+t)^2 + Nr_m \arcsin\left(\frac{a}{A}\right)\sqrt{A^2-a^2} - N(a+t)(\frac{ar_m}{A}+t) \right] \varphi(a)\,da , \qquad (1) $$

where $A = a + t + r_m$, a is the particle radius, ρ is the true density of material, N is the average coordination number of nanoparticles in aggregates, t is the thickness of an adsorbed nitrogen layer, and r_m is the meniscus radius determined at $0.05 < p/p_0 < 0.2$ corresponding to the effective radius R of voids between spherical NPNP. Condition $S_\varphi = S_{BET}$ could be used to estimate the N value. An additional criterion $|<S_\varphi> - S_{BET}| < 1$ m^2/g could be applied to determine the $a_{\min}$ and $a_{\max}$ values upon the $\varphi(a)$ computation at $p/p_0 < 0.4$ (*i.e.,* before capillary condensation starts) with equation

$$ <S_\phi> = \iint S_\phi(r_m,t)\,dt\,dr_m / \iint dt\,dr_m . \qquad (2) $$

Note that the PaSD $\varphi(a)$ could be also determined using small angle X–ray scattering (SAXS), high-resolution transmission electron microscopy and other methods to check the SSA values determined from the adsorption data [8–17]. In the mentioned approach using Eqs. (1) and (2), the S_{BET} value is used as an important parameter to compute the $<S_\varphi>$ value; therefore, the computation of the S_{BET} value should be maximum reliable. This is one of the reasons of this study. The second aspect of the study is linked to the analysis of the BET method application to a large set (about 200 samples) of very different adsorbents such as fumed oxides initial and modified, porous silicas, activated carbons and polymers, to elucidate a possible range of errors and some corrections of the $\sigma_m(N_2)$ and S_{BET} values dependent on a type of adsorbents.

MATERIALS

Six types of materials at the S_{BET} values in the 3–3463 m^2/g range analyzed here: fumed silicas

The specific surface area (S_φ) of fumed metal or metalloid oxides (silica, alumina, titania, *etc.*) composed of NPNP characterized by certain particle size distributions, PaSD $\varphi(a)$ (computed using a self–consistent regularization (SCR) procedure for the pore size distributions, PSD $f_V(R)$ and PaSD $\varphi(a)$ with a model of voids between spherical NPNP) could be computed with equation [8–15]

(38 samples, Pilot plant of the Chuiko Institute of Surface Chemistry (CISC), Kalush, Ukraine, Degussa, Evonik, Wacker, Cabot, and Nippon Aerosil) and porous silicas (24 samples, (Merck, Crosfield, and CISC), alumina, titania and complex binary and ternary nanooxides (62 samples, CISC), modified nanosilicas (36 samples, CISC), chars and activated carbons (18 samples, MAST Carbon (UK), PSO MASKPOL (Poland), HPSD (Hajnówka, Poland)), and porous polymers (36 samples, Purolite, Merck, Fluka, Rohm and Haas (Philadelphia, USA), Maria Curie-Skłodowska University (MCSU, Lublin, Poland), and CISC). More detailed information on the used materials is given elsewhere [8–17].

NITROGEN ADSORPTION

The adsorption of nitrogen has been used to evaluate the accessible specific surface area (SSA), S_{BET} [1–3]. The nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2010, 2020, 2405N, or 2420 and Quantachrome Autosorb adsorption analyzers) were recorded for samples degassed at 80–100 °C (polymers and some modified silicas) or 150–200 °C (disperse and porous oxides and carbons) for several hours.
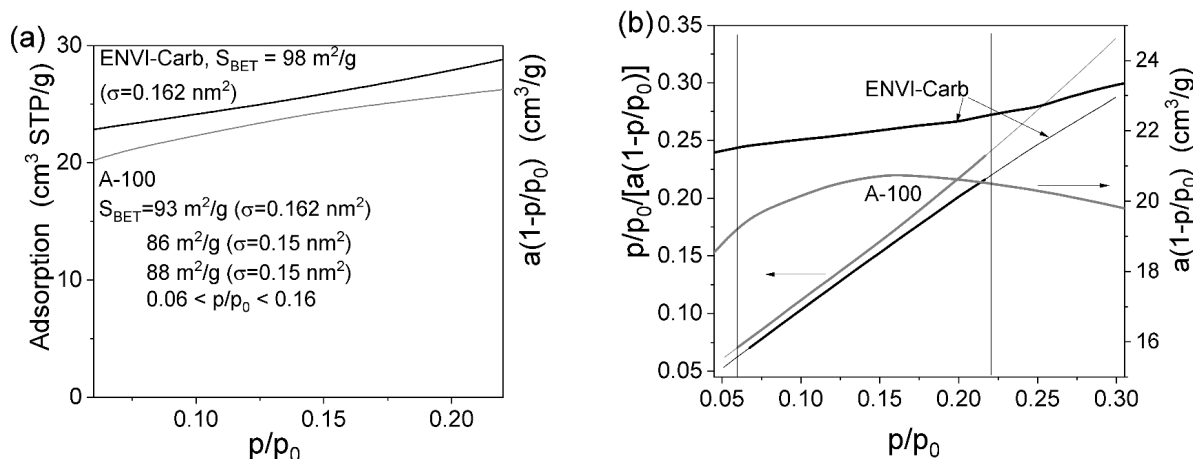
RESULTS AND DISCUSSION

Graphitized carbon ENVI–Carb (Supelco, Bellefonte, particles of 40–60 μm in diameter) is described by the firm as a non-porous carbon. The absence of pores is related to nonporous nanoparticles (NP) of 20–40 nm in size (estimated here from the SSA value). Note that activated carbons (AC) could be composed of nanoparticles of similar sizes, but these nanoparticles are nano- or nano/mesoporous in contrast to those of

ENVI–Carb. For ENVI–Carb and AC, nanoparticles form aggregates relatively tightly packed. Voids between NP in compacted microparticles provide meso/macropores in carbon materials. The absence of nanopores and the surface nature of graphitized particles of ENVI–Carb at a relatively small SSA value (~100 m^2/g) allow one to assume that the $\sigma_m(N_2)$ value could be equal to 0.162 nm^2 for this adsorbent (at parallel-to-surface adsorption of the N_2 molecules in the complete monolayer). Additionally, the c_{BET} value equal to 109.4 (at $0.05 < p/p_0 < 0.3$) is quite appropriate, as well as increasing $a \times (1–p/p_0)$ *vs.* p/p_0 in the range of $p/p_0 = 0.05–0.3$ (Fig. 1 *b*), for the use of the BET method. Therefore, we could assume that the S_{BET} value of ENVI–Carb is accurately computed and could be used for comparison of the normalized (per m^2 instead of gram) nitrogen adsorption isotherm to those for various adsorbents (Figs. 1–4). One could assume that if the $\sigma_m(N_2)$ value is equal to 0.162 nm^2 for a certain adsorbent that the normalized adsorption isotherm (in cm^3 STP/m^2) for this adsorbent in the BET range should be close to that of ENVI–Carb. If there is a certain difference between the normalized isotherms for an adsorbent and ENVI–Carb that the effective value of $\sigma_m(N_2)$ for the former differs from the standard one (0.162 nm^2) due to the orientation effects or overlapping monolayer and

multilayer adsorption. The $\sigma_m(N_2)$ value could be really smaller than 0.162 nm^2 due to the orientation effects for nitrogen molecules adsorbed onto functionalized surfaces, but it could not be larger than 0.162 nm^2. However, overlapping monolayer and multilayer adsorption causes apparent underestimation of the value of $\sigma_m(N_2) = 0.162$ nm^2 (*vide infra*).

The first comparison (Fig. 1) could be done for fumed silica A−100 having nonporous NP and the SSA value close to that of ENVI–Carb. However, the surface silanol groups affect the orientation of the N_2 molecules adsorbed at the A−100 NP surface [9]. Therefore, the effective value of $\sigma_m(N_2)$ is diminished, and the use of $\sigma_m(N_2) = 0.162$ nm^2 results in overestimation of the SSA value by *ca.* 8 % for A−100 (Fig. 1). Note that the use of the p/p_0 range of 0.06–0.22 (Fig. 1 *b*) results in the SSA values of 99 and 92 m^2/g for ENVI–Carb and A−100, respectively, at $\sigma_m(N_2) = 0.162$ nm^2. However, for A−100, the criterion of increasing $a \times (1–p/p_0)$ *vs.* p/p_0 is true in a narrower range of $p/p_0 = 0.05–0.16$ (Fig. 1 *b*). Clearly, the use of the smaller p/p_0 range results in a smaller deviation from the linear approximation for $p/p_0/[a \times (1–p/p_0)]$ *vs.* p/p_0 (Figs. 1 *b* and 2) used to estimate the S_{BET} values. Note that this deviation could be relatively large, especially for adsorbents with nanopores or narrow mesopores (Figs. 2 *b* and 3 *b*).
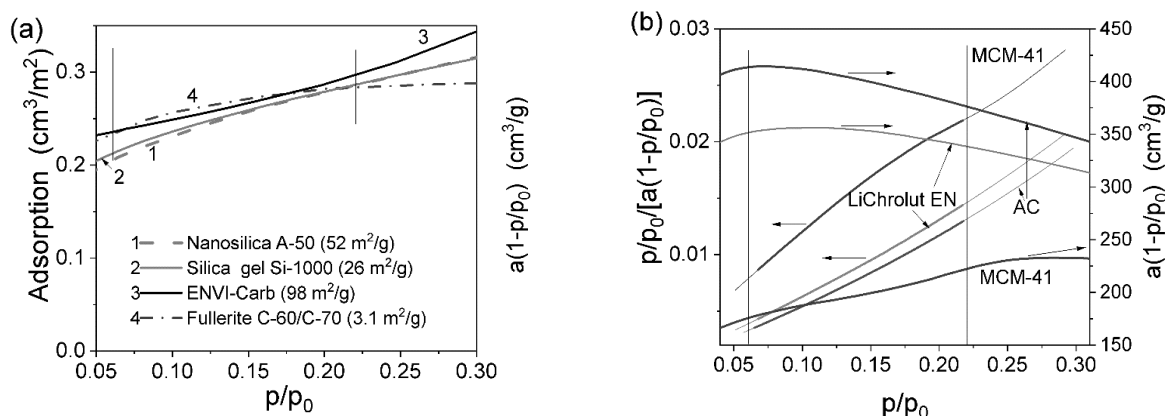

Fig. 1. Parts of nitrogen adsorption isotherms for graphitized carbon black ENVI–Carb and fumed silica A−100: (*a*) standard at $p/p_0 = 0.06–0.22$ and (*b*) linearized shape at $p/p_0 = 0.06–0.22$ and 0.05–0.3 used in the BET equation and criterion curves of $a \times (1–p/p_0)$ *vs.* p/p_0 (it increases for ENVI–Carb in the total BET range, but for A−100, it increases in a narrower range of $p/p_0 = 0.05–0.16$)

An increase in the S_{BET} value of AC (Fig. 3) could not lead to the appearance of the negative c_{BET} values if contribution of mesopores increases and a nanopore peak in the pore size distribution (PSD) is located at half-width $x > 0.5$ nm (Fig. 3 *c*), and increasing $a \times (1-p/p_0)$ *vs.* p/p_0 is true in the BET range (Fig. 3 *b*). Note that at $x > 0.35$ nm, it is possible to adsorb the nitrogen monolayer on both walls of pores. If $x < 0.35$ nm, the adsorption of two nitrogen layers is impossible. In this case, the nitrogen molecules can be located non-parallel-to-surface to interact with both pore walls, because the verical position or non-parallel-to-surface one provide more complete infilling of narrow nanopores than that at parallel-to-surface location. This aspect is one of the reasons of the BET application problems to nanoporous adsorbents. The difference in the S_{BET} and S_{NLDFT} (determined using the nonlocal density functional theory (NLDFT) method) values is in the range of 14.6–17.9 % for selected AC shown in Fig. 3. This suggests that the S_{BET} value could be significantly overestimated for AC, especially with a significant contribution of nanopores (Fig. 3 *c*). For mainly nanoporous AC (Fig. 3, curves 1 and 2), the c_{BET} value is negative (Fig. 3 *b*) and increasing $a \times (1-p/p_0)$ *vs.* p/p_0 is only at $p/p_0 = 0.05–0.1$; *i.e.*, the use of the BET theory is questionable for these AC in contract to nano/mesoporous AC (Fig. 3, curves 3 and 4).

For adsorbents composed of nonporous NP, *e.g.*, fumed oxides initial or modified, the use of standard $\sigma_m(N_2)$ value results in the overestimation of the S_{BET} value (see location of the adsorption curves with respect to that of ENVI–Carb, Fig. 4 *a*, *b*, *d*). This is due to non-parallel-to-surface orientation of the molecules from the first monolayer. Therefore, the nitrogen adsorption isotherms normalized to the adsorption per m^2 (dividing standard adsorption in cm^3 STP/g by the S_{BET} value giving the values in cm^3 STP/m^2) for these adsorbents are located below that for ENVI–Carb (Fig. 4 *a*, *b*, *d*).
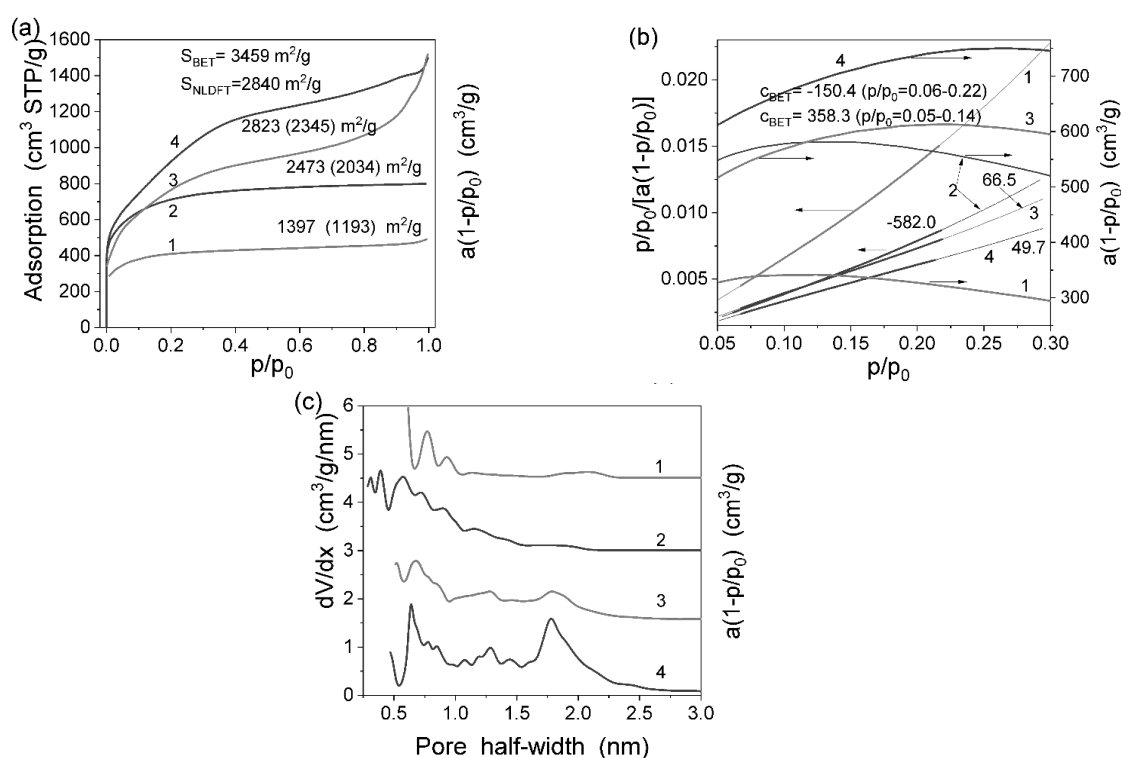

Fig. 2. Parts of nitrogen adsorption isotherms for various adsorbents at p/p_0: (*a*, *b*) 0.05–0.3 and 0.06–0.22; (*b*) mesoporous ordered silica MCM–41 ($S_{BET} = 1054$ and 1107 m^2/g for the short ($a(1-p/p_0)$ increases in this range) and long p/p_0 ranges, respectively, at $\sigma_m = 0.162$ nm^2 $S_{BET} = 911$ m^2/g but 957 m^2/g at $\sigma_m = 0.14$ nm^2), porous polymer LiChrolut EN ($S_{BET} = 1464$ and 1383 m^2/g for the short and long p/p_0 ranges, respectively, at $\sigma_m = 0.162$ nm^2), and activated carbon ($S_{BET} = 1600$ and 1482 m^2/g for short and long p/p_0 ranges, respectively, at $\sigma_m = 0.162$ nm^2)

For adsorbents composed of porous NP (*e.g.*, AC, Fig. 4 *e*) or having nanopores and narrow mesopores (porous silicas, Fig. 4 *c* and porous polymers, Fig. 4 *f*), the normalized adsorption isotherms could be located both above and below the isotherm for ENVI–Carb in the BET range. The effect of the use of the standard $\sigma_m(N_2)$ value (0.162 nm^2) is the same (*i.e.*, the overestimation of the S_{BET} value) for fumed silicas and complex nanooxides or mesoporous silicas. This is due to changes in the orientation of the N$_2$ molecules, which can be slightly polarized upon interaction with polar surface functionalities. Apparently underestimated $\sigma_m(N_2)$ value is due to the overlapping monolayer and multilayer sorption, *e.g.*, for MCM–41 characterized by $c_{BET} = 29.7$ (at $0.06 < p/p_0 < 0.22$) corresponding to the mentioned overlap. For washed-out Lichrolut EN (curve is located above and below the curve for ENVI–Carb, Fig. 4 *f*), $c_{BET} = -162.0$ and 438.4 at

p/p_0 = 0.06–0.22 and 0.05–0.14, respectively, and $a \times (1–p/p_0)$ decreases with p/p_0 in the BET range (Fig. 2 *b*). Therefore, the BET method appropriation is questionable for this adsorbent (however, S_{NLDFT} = 1408 m²/g corresponds to 1.8 % deviation for S_{BET}), as well as for nanoporous AC shown in Fig. 3 (samples 1 and 2). Similar results are for some other activated carbons possessing nanopores and narrow mesopores (Fig. 4 *e*). For AC (Fig. 2 *b*), c_{BET} = −84.8 (at 0.06 < p/p_0 < 0.22), $a \times (1–p/p_0)$ decreases with p/p_0 in the BET range, and the normalized curve (in the BET range) is close to that

of LiChrolut EN and located at much lower values (*ca.* by an order of magnitude) than that for ENVI–Carb (Fig. 1 *b*). For this AC, c_{BET} < 0 even in the minimal p/p_0 range (0.05–0.14) because it is practically pure nanoporous. For similar cases, there are some general recommendations [5] on the estimation of the SSA values, *e.g.*, the use of CO_2 or benzene adsorption at room temperature or, at least, the use of the S_{NLDFT} values instead of S_{BET} that is of importance from a practical point of view [18–27]. However, in the case of the presence of a number of polar surface sites, the use of CO_2 as a polarizable probe is not recommended [5].
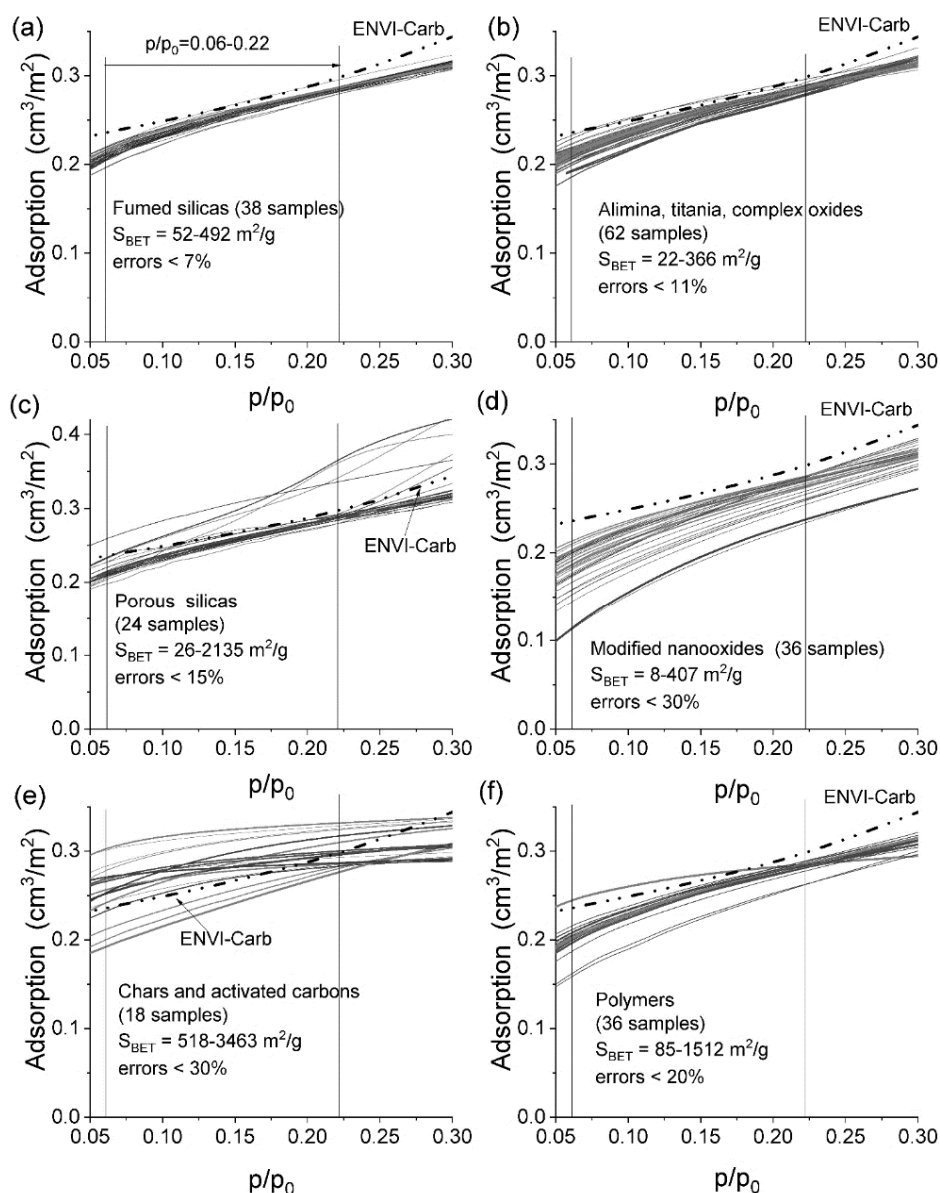

Fig. 3. *a* – Nitrogen adsorption isotherms for four activated carbons (the values of S_{BET} and S_{NLDFT} are shown); *b* – BET plot (c_{BET} values are shown for carbon 1) and criterion curves of $a \times (1−p/p_0)$ *vs.* p/p_0; (*c*) nonlocal DFT pore size distributions for these AC samples. $a \times (1–p/p_0)$ mainly decreases in the BET range for AC 1 and 2, but it increases in the short BET range (0.06–0.22) for AC 3 and 4

The SSA values as well as other textural characteristics could be also calculated using the SAXS method [12, 15, 17, 28–33]. However, the S_{SAXS} value includes a surface area of both open (accessible for adsorbates) and closed (inaccessible for adsorbates) pores and it could be much larger than the S_{BET} value, especially for chars or AC with a low activation (burn-off) degree. If the closed pores are absent (*e.g.*, nanooxides, silica gels) that the values of S_{SAXS}

and S_{BET} could be similar [33], but it depends on the particulate morphology. For example, for fumed silica A–300, S_{SAXS} = 331 m²/g, S_{BET} = 294 m²/g (N_2), and SSA estimated from the average NP size (SAXS model of spherical particles) is $S_{SAXS,d}$ = 286 m²/g [12, 15, 34]. The value of S_{SAXS} is larger than S_{BET} because the SSA accessible for the N_2 molecules is smaller than the total surface area (accessible for X–ray scattering) of NP due to the NP aggregation. Additionally,

NP are composed of proto-particles (nuclei formed in the flame and then stick together in the flame to form NP with subsequent deposition of silica layers), which have boundaries in NP interior causing additional X–ray scattering. There is also the NP form-factor effect because NP have non-ideal spherical-like shapes; therefore, $S_{SAXS,d} < S_{SAXS}$. Note that the values of

$S_{SAXS,d}$ and $<S_\varphi>$ calculated with Eq. (2) (or S_{BET}) are similar for A−300, since the difference is smaller than 3 %. In other words, the SAXS method, as well as the BET, DFT, *etc.*, has certain features, which should be considered upon accurate morphological and textural analyses of various adsorbents.

Fig. 4. Parts of nitrogen adsorption isotherms for various adsorbents at $p/p_0 = 0.05–0.3$ and 0.06–0.22: (*a*) fumed silicas; (*b*) fumed alumina and titania and complex binary and ternary nanooxides with silica, alumina, and titania initial and after chemical vapor deposition of titania onto nanosilica; (*c*) porous silicas; (*d*) nanosilicas modified by various silanes and high-molecular weight compounds (polymers and proteins); (*e*) chars and activated carbons; and (*f*) porous polymers

Thus, for various adsorbents and probe adsorbates, there are several factors affecting the accuracy and reliability of the results obtaining upon the analyses of the adsorption isotherms and

other related morphological, textural, and structural data [2–27, 34]. This depends not only on the sizes and shapes of pores but also on the nature of adsorbent surfaces and probe molecules, particulate morphology of adsorbents, as well as on the computation methods applied to the experimental data [2–34].

CONCLUSION

A problem of the applicability of the Brunauer–Emmett–Teller (BET) method using nitrogen as a probe adsorbate is well known for various adsorbents, especially for nanoporous carbons. Therefore, the nitrogen adsorption isotherms in the range of the BET method (p/p_0 = 0.05–0.3, 0.06–0.22 or smaller) are analyzed here for a large set (about 200 samples) of different adsorbents such as fumed oxides (individual, binary and ternary, initial and modified), porous silicas, activated carbons, and porous polymers. Graphitized carbon black ENVI–Carb composed of nonporous nanoparticles aggregated into microparticles is used as a standard adsorbent characterized by the standard surface area occupied by a nitrogen molecule $\sigma_m(N_2)$ = 0.162 nm^2. For initial nanooxide adsorbents, such as silica, alumina, titania and complex ones, composed of nonporous nanoparticles, the value of $\sigma_m(N_2)$ = 0.162 nm^2 (and, therefore, S_{BET} value) is overestimated by *ca.* 10 % because of nonplanar orientation (at a surface) of the N_2 molecules adsorbed in the first monolayer and slightly polarized due to interactions with polar surface functionalities (*e.g.*, various hydroxyls). For nanooxides modified by low-molecular (various silanes) and high-molecular (linear, 2D and 3D polymers and proteins) compounds, the overestimation of the S_{BET} value could reach 30 %, as well as for some AC. For adsorbents possessing nanopores (half-width x or radius R < 1 nm) or narrow mesopores (1 nm < R < 3 nm), an overlap of monolayer and multilayer adsorption results in apparent underestimation of σ_m. Nonplanar orientation of the N_2 molecules results in overestimation of S_{BET}. These effects could lead to various location of the normalized (by dividing by S_{BET}) nitrogen adsorption isotherms (in the BET range) with respect to that for ENVI–Carb. Some of the adsorbents are characterized by negative values of c_{BET} and decreasing $a \times (1–p/p_0)$ *vs.* p/p_0 in the BET range. The negative results based on both criteria suggest the inapplicability of the BET method (with nitrogen as a probe) for the accurate textural analysis of the adsorbents, *e.g.*, characterized by the main contribution of nanopores. For these adsorbents, the overestimation of the S_{BET} values, *e.g.*, in comparison to the S_{NLDFT} values, is quite characteristic. Thus, typically, the S_{BET} values determined from the nitrogen adsorption isotherms could be frequently overestimated due to two main effects: (i) non-parallel-to-surface orientation of the N_2 molecules, and (ii) an overlap of monolayer and multilayer adsorption with infilling of nanopores at low pressures. These aspects should be considered and controlled for maximum accurate textural characterization of various adsorbents, especially nanoporous ones, that is of importance from a practical point of view.

Особливості використання методу БЕТ для різних адсорбентів

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Існує проблема придатності методу Брунауера-Еммета-Теллера (БЕТ) з використанням азоту як адсорбату для різних адсорбентів, в особливості нанопористих. Тому ізотерми адсорбції азоту в діапазоні методу БЕТ ($0.05 < p/p_0 < 0.3$ та $0.06 < p/p_0 < 0.22$) проаналізовано для великої кількості (приблизно 200 зразків) різних адсорбентів, таких, як пірогенні оксиди (індивідуальні, бінарні та потрійні, вихідні та модифіковані), пористі кремнеземи, активоване вугілля та пористі полімери. Графітизовану сажу ENVI–Carb, що складається з непористих наночастинок, щільно агрегованих у мікрочастинки, використано як стандартний адсорбент зі стандартною площею поверхні, яку займає молекула азоту $\sigma_m(N_2) = 0.162$ нм². Для вихідних нанооксидів, що складаються з непористих наночастинок, величина $\sigma_m(N_2) = 0.162$ нм² є завищеною, тобто $S_{БЕТ}$ завищена, приблизно на 10 % внаслідок орієнтації молекул азоту не паралельно поверхні при їх взаємодії з різними полярними поверхневими групами (гідроксилами). Для нанооксидів, модифікованих низько-молекулярними (силанами) та високомолекулярними (лінійними, 2D та 3D полімерами та білками) сполуками, $\sigma_m = 0.162$ нм² (та $S_{БЕТ}$) може бути завищеною на величину до 30 %. Для адсорбентів, що мають нанопори (напівширина чи радіус пор $R < 1$ нм) чи вузькі мезопори (1 нм $< R < 3$ нм), перекриття процесів мономолекулярної та полімолекулярної адсорбції (що дає уявно більшу σ_m) та непланарна орієнтація молекул N_2 (що дає меншу величину σ_m) можуть призводити до різної локалізації нормованих (поділених на $S_{БЕТ}$) ізотерм адсорбції азоту (в БЕТ діапазоні) щодо розташування нормованої ізотерми для ENVI–Carb, які характеризуються різними величинами $c_{БЕТ}$. Два головних критерії непридатності чи придатності методу БЕТ (з азотом як адсорбатом) на основі величини $c_{БЕТ}$ та залежності $a \times (1 - p/p_0)$ від p/p_0 в інтервалі БЕТ можуть давати неузгоджені оцінки для адсорбентів, які не є чисто нанопористими, проте ці оцінки практично завжди узгоджені для нанопористих чи мезо/макропористих адсорбентів.

Ключові слова: *ізотерми адсорбції азоту, обмеження методу Брунауера–Еммета–Теллера, нанооксиди, пористі кремнеземи, вуглеці, пористі полімери*

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