Generalized variables for both porous and ordered mesoporous materials

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Abstract

This work is a continuation of our previously published work (Titelman in J Porous Mater 19:1–13, 2012), where generalized variables for the synthesis of porous materials were proposed: processing X and structural Y . X represents the route of the entire production process and covers the complete set of individual variables, both quantitative and qualitative. This paper proposes a concept of equivalent X -s, that is, routes leading to equal values of the property of interest. Examples of equivalent X are given. The most economical route can be chosen. $Y = V_w/V_p$ (the ratio of the apparent volume of the walls to the total volume of open pores) is the structural parameter of the ordered mesoporous materials (OMMs), more sensitive than the wall thickness. For OMMs a formula is proposed for estimating V_w ; this is the product of the total surface area S_{BET} and the wall thickness t . Now the Y covers all parameters of OMM. Excluding the volume V_{sk} of the skeleton from V_w , we obtain the volume V_{iw} of inaccessible intrawall pores; the size effect (Vradman et al. in Microporous Mesoporous Mater 93:313–317, 2006) on V_{iw} was discovered. The specific length of the adsorbate body L_v proposed in Titelman (2012) is supplemented by the length of the surface area of the adsorbent L_s and the equation relating the hydraulic diameter D_h to the average pore diameter D_p is obtained. The known $D_h = 4V_p/S_{\text{BET}}$ is equal to D_p , only if $L_v = L_s$. D_h is considered as a diameter of pores with smooth walls, and L_s/L_v —as a roughness factor. Application of the proposed parameters gives a new insight of many published results.

Graphic abstract Presentation of equivalent processing variables (routes); roughness factor as result of new derivation of hydraulic pore diameter and size effect on intrawall void space.

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Equivalent process routes: numbers - synthesis temperature, °C, aging temperature, °C, aging time, h, correspondingly (data from [15], picture from Lightwise)

$D_p/D_h = L_s/L_v$ - roughness factor, D_h - hydraulic diameter, L - pore length

t - wall thickness, D_p - average pore diameter. $V_w = S_{BET} \cdot t$ - apparent wall volume, V_{iw} - intrawall void space, V_{sk} - wall skeletal volume (based on [19] data).

Keywords Generalized variable · Equivalent variables · Roughness factor · Wall volume · Intrawall porosity

1 Introduction

Previously proposed for ordered mesoporous materials (OMM) [1], the generalized variable X of many-factorial processes, the generalized structural parameter of the porous material Y , data sorting by property as a key, the specific length of pores L_v and the size effect on microporosity [2] were applied to many published (including own) data and gave new noteworthy results.

It was previously noted [1, Table 4] that after tableting powders of some OMM under high pressure [3], the parameter of the unit cell a_o and the pore diameter D_p did not change. It was shown [1, Table 5] that the constancy of the radial pore sizes was compensated by a change in the newly proposed structural parameter: the axial pore size, namely the specific length L_v of the adsorbate body. For L_v , only data from regular adsorption-desorption tests are needed: total pore volume V_p and average pore diameter D_p . Naturally, all the assumptions made during the calculations of V_p and D_p refer to L_v .

The pressure in [3] was the only processing variable. This has led to the search for the equality of various structural parameters of porous materials in multi-factorial processes, and the paths leading to the same values of the parameters—the goal number 1 of this article.

Calculations L_v questioned the nuances of obtaining [4] the well-known formula for hydraulic pore diameter $D_h = 4V_p/S_{BET}$ (S_{BET} is the total surface area of pores), which is still used to estimate the average pore diameter D_p [5], but this is not always true; see, for example, [6–8].

According to the classical hydrodynamic definition, the hydraulic diameter is 4 times the ratio of the cross-sectional area A of the channel to the perimeter U of the wetted surface, that is, $D_h = 4A/U$. When the free-form channel was modeled by a straight ring channel, where $U = \pi D$, this ratio led to $A = \pi D^2/4$. To go from the hydrodynamic definition of D_h to the “adsorption” one, we must express D_h in terms of the total adsorbate volume V_p and the total surface area S_{BET} . Both the cross-sectional area of the pores $\pi D_p^2/4$ and the perimeter πD_p were multiplied by the same pore length L , and the formula $D_h = 4V_p/S_{BET}$ [4] appeared. For real pores, this equation must be corrected, since in the general case the length of the adsorbate body along its axis and along its surface (or the surface of the adjacent walls of the adsorbent) are not equal. The proof of this statement is the well-known roughness of the surface of the pore walls (waviness, tortuosity, corrugation, fractality, fragmentation). The new derivation of the formula for D_h and the demonstration of its new function is goal number 2 of the article.

The generalized dependent structural variable $Y = V_w/V_p$ (V_w is the apparent volume of the walls) represents the overall structure of the material [1]. A similar parameter is the total porosity P_o ($P_o = V_p/(V_p + V_w)$). Any change to any x of the preparing process should affect V_w , or V_p , or both of them; if V_w/V_p does not change, an internal “reconstruction” of the structure occurs. The last statement is very clear from Schmidt-Winkel et al. data (9, ESM-1), where the porosity P_o remained constant (for example, 84%) at 10

different X , while other properties (D_p , S_{BET}) underwent changes.

V_w includes the volume of the true (skeletal) material V_{sk} plus the volume of closed and unavailable for adsorption intra-wall pores V_{iw} . Raising a V_{iw} may not be desirable; the smaller V_{iw} and, respectively, V_w , the more material (by weight) can fit in the reactor. The ratio V_{iw}/V_p shows what volume of intrawall pores was obtained for 1 volume of open pores. At the same time, intrawall porosity can create a structure of struts providing high mechanical strength of the walls [1]. Unfortunately, data on V_w (or apparent density $\rho_w = 1/V_w$) are missing in the literature. This can be obtained from the total porosity P_o , but P_o is also very rare. One of such rare works [9] was discussed earlier [1]. The apparent wall density ρ_w calculated by P_o was in the range of 2.17–2.28 g/cm³. The true density of silica is 2.2 g/cm³ [10], and the values obtained are realistic and indicate that large-pore silica foams have very dense walls. Thus, there is a need for a method for determining V_w —goal number 3 of this work.

Under certain conditions, V_w/V_p can be reduced to t/D_p [1], which represents the stress-induced mechanism of microporosity (size effect on it [2]) and complements the porosity caused by the pore-forming polymer [11]. The question is, whether t/D_p also affects the intrawall porosity V_{iw} —goal number 4 of the article.

The mentioned parameters, dependencies and methods can be used for looking for the best properties of heterogeneous catalysts and sorbent in many-factorial processes preparing them.

2 Equivalent generalized variables X-s

It is known that in crystals all physical properties are interrelated, and a change in a certain property can be caused by various factors. In addition, the observed variables can cause phenomena that we do not see, but which also affect the material. The scheme of interrelation and equilibrium of physical properties of crystals is clearly demonstrated in the textbook [12, p. 275, Fig. 238]. It can be assumed that the mutual influence of factors and properties also exist in porous materials. Moreover, the effect may be synergistic. For example, Ikonnikov, Titelman et al. [13] showed that the maximum enhancement of granular ZnO sorbent was obtained by adding a mixture of hydrophobic polymers (polyvinyl alcohol and dextrin) in a certain ratio. Besides the technological and operational factors can effect selectively on the properties of porous materials [14]. Based on these considerations, the generalized independent variable X (or route #) will be a useful tool: in a many-factorial process, it covers the full set of observable

individual variables (x_1 , x_2 , etc., both quantitative and qualitative) of material synthesis and post-synthesis operations, affecting the properties of the final material.

As a rule, we choose X for the property of interest. The property of interest may be: (1) for heterogeneous catalysis—a large total surface area S_{BET} , (2) for adsorption—a large pore volume V_p , (3) for separation—a width of pore diameter D_p , (4) for Ordered Materials—wall thickness t . In any study, sorting the data in the table according to the property of interest as a key, we modify the table so that the routes are arranged in ascending (decreasing) influence of the combination of variables on this property. Equivalent routes give equal property values. For example, Klimova et al. [15] prepared 8 samples (8 syntheses or X) of ordered mesoporous silica SBA-15, varying 3 factors: x_1 —synthesis temperature (35 and 60 °C), x_2 —aging temperature (60 and 80 °C) and x_3 —aging time (24 and 48 h). Thus, X is a combination (x_1 – x_2 – x_3). The measured properties were: unit cell parameter a_o , specific surface area S_{BET} , specific pore volume V_p , and average pore diameter D_p . We added the wall thickness $t = a_o - D_p$ and sorted the data for each of the mentioned properties as a key. In sorted data, the same (or close) values are located next to each other, and their preparation conditions (technological routes X) are easy to compare. The obtained tables (ESM-2, part 1) clearly showed that among 8 runs, 3 give equal a_o , the other 3 give equal D_p ; equal for 2 runs t were obtained twice. For example, the same unit cell parameter $a_o = 10.6$ nm was obtained as a result of combinations: X_3 (run 3: 60 °C–60 °C–24 h), X_6 (run 6: 35 °C–80 °C–24 h) and X_8 (run 8: 60 °C–60 °C–48 h). Thus, such X -s are equivalent for obtaining this a_o . Equivalent X data suggest the mutual influence of individual factors x . This case of constancy a_o was, as before [1], compensated by different specific pore lengths; related to X_3 , X_6 and X_8 , the relative $L_{v3}:L_{v6}:L_{v8}$ were 1:1.16:1.24. Even more differences show pore volumes; relative $V_{p3}:V_{p6}:V_{p8}$ were 1:1.16:1.35.

Schmidt-Winkel et al. [9] synthesized ordered silica foams. X includes: x_1 —TBM/P123 ratio (range 0.3–2.5; TMB—organic swelling agent 1,3,5-trimethylbenzene; Pluronic P123—structure-forming non-ionic block copolymer), x_2 —aging temperature (100 and 120 °C), x_3 —adding NH_4F (“with” and “without”, affects the window size). Three equivalent X -s provide a total porosity of $P_o = 80\%$, the other 10 X -s gave $P_o = 82\%$, and another series in 10 X -s led to $P_o = 84\%$. At the same time, other properties (D_p , S_{BET} , etc.) within these groups undergo changes (ESM-1). Among the equivalent combinations of X -s, we can choose the most economical. For example, from the mentioned above [15 Klimova] x_1 – x_2 – x_3 combinations of SBA-15 synthesis with pore diameter $D_p = 6.5$ nm, namely: (1) 60 °C–60 °C–24 h, (2) 35 °C–80 °C–24 h and (3)

60 °C–60 °C–48 h in terms of energy savings, the first combination will be best. As if 3 roads lead to the same intersection (graphic abstract), but one of the roads is better.

3 The equation relating the average pore diameter to the hydraulic diameter

In our previous work [1], the volume of the adsorbate layer V_p (at the full condensation pressure N_2) was used to estimate the specific length $L_v = V_p / ((\pi/4) D_p^2)$ along the body axis of the adsorbate. Now let's also calculate the specific length L_s of the surface of the adsorbate layer, which wets the surface S_{BET} of the adsorbent: $L_s = S_{BET} / \pi D_p$. These two lengths allow us to refine the formula for the hydraulic diameter of the adsorbent D_h , given in the book [4], and find the relationship of D_h with D_p .

The cross-sectional area $\pi D_p^2/4$ and the perimeter πD_p of the adsorbate body inside straight round pores of 1 g of the porous material should be multiplied instead of the unspecified L in [4] by the corresponding lengths: (1) the cross-sectional area should be multiplied by the specific length of the adsorbate body L_v to get $V_p = L_v \cdot \pi D_p^2/4$, (2) the perimeter of the adsorbate body should be multiplied by the specific length L_s of the wetted surface to get $S_{BET} = \pi D_p \cdot L_s$. We find

$$D_p = (4V_p/S_{BET}) (L_s/L_v) = D_h (L_s/L_v) \quad (1)$$

and, therefore, the average pore diameter D_p will be equal to the hydrodynamic diameter $D_h = 4V_p/S_{BET}$, if (for 1 g of the adsorbent) the length of the adsorbate layer L_v and the length of the wetted surface of the adsorbent wall L_s are equal, i.e. $(L_s/L_v) = 1$. In other words, D_h can be used as D_p only if $(L_s/L_v) = 1$. The differences shown in the mentioned works [6–8] are cases of absence of this equality. Generally speaking, D_h is simply a diameter of a family of pores with an equal $4V_p/S_{BET}$ ratio.

Equation 1 introduces the concept of a smooth and rough surface of the pore walls in a natural way. The equality $L_s = L_v$ means that the surface of the adsorbent wrapped around the layer of adsorbate is smooth. Such a pore with a diameter of D_h can be considered as a diameter of pores with smooth walls that can be used as an intrinsic *reference* of pores with smooth walls for any real pore. Thus,

the internal standard of a porous material with smooth walls is a direct pore having a diameter of $D_h = 4V_p/S_{BET}$. In turn, the inequality $L_s \neq L_v$ or $(L_s/L_v) \neq 1$ indicates the surface roughness.

Consider the cases when $(L_s/L_v) \neq 1$. The case $L_s > L_v$ means waviness, the tortuosity of the surface of the walls, while the case $L_s < L_v$ means the fragmentation of the surface; both cases indicate a certain roughness of the walls. Therefore, $(L_s/L_v) = D_p/D_h$ can be called the roughness factor. We accept the term “roughness” in accordance with the Chorkendorff and Niemantsverdieht model [16, p. 183], which distinguishes microporosity and surface roughness in relation to pore depth and pore width: deep pores cause microporosity, and shallow pores produce roughness. Below we confirm this choice by the absence of a correlation between (L_s/L_v) and the surface area of micropores.

From Eq. 1 it follows that D_h does not exclude any known theory of adsorption for D_p . In contrast, the roughness factor in the form of D_p/D_h is a certain dimensionless number that connects two estimates of the average pore diameter of the same sample: D_h from the hydrodynamic model and D_p from some adsorption model.

By analogy with the real walls of the pores, one can imagine a piece of cut but not cleaned tree. The length of the bark L_s may be greater than the distance between slices L_v . If the bark is partially cleaned (fragmentary surface), L_s will be less than L_v . For example, all 6 host/guest CoSBA-15 [17] samples have $L_s/L_v < 1$.

L_s/L_v is *generalized parameter* because it covers the main single parameters S_{BET} , V_p and D_p of any porous material.

A certain coefficient of roughness R_f was proposed by Zukal et al. [18] in the form of the ratio of the true and geometric surfaces. To control the roughness, the rough surface of the SBA-15 pore walls was smoothed by post-synthetic coating of the mesoporous silica SBA-15 with aluminum from an aqueous solution of aluminum chlorhydrol. The coefficient L_s/L_v was calculated using their S_{BET} , V_p and D_p . Table 1 shows the dependences of both factors on the concentration C , % aluminum chlorhydrol in solution.

From the values of R_f it follows that with an increase in the Al content, the roughness smoothly decreases, and only the last sample becomes smooth ($R_f = 0.99$). The coefficient L_s/L_v behaves differently: the smoothest (even) sample ($L_s/L_v = 1.01$) is formed with an 8% smoothing solution. The following increase in C leads

Table 1 Surface smoothing SBA-15. Effect of aluminum chlorhydrol concentration in the grafting solution C , %, on two roughness factors: R_f of Zukal et al. [18] and our L_s/L_v . With the permission of CCC 2019

C (%)	0	1.6	4	8	16	32	48	64
R_f	1.25	1.25	1.22	1.17	1.07	1.05	1.03	0.99
L_s/L_v	1.38	1.36	1.22	1.01	1.04	1.06	1.06	1.05

to the appearance of a new small roughness, presumably due to the appearance—alignment of the hillocks of the aluminum layer. It should be emphasized that, in contrast to R_f , which is based only on surfaces, the coefficient L_s/L_v is based on 3 basic parameters of porous materials: pore surface, volume, and radial size. However, it is possible that the effectiveness of various processes on Al-SBA-15 will correlate with various roughness factors.

4 OMMs: the apparent volume of the pore walls V_w and the intrawall volume of the closed pores V_{iw}

The following formula for estimating V_w is based on the simple consideration that any wall has a surface, or any surface belongs to a certain wall:

$$V_w = St, \text{ cm}^3/\text{g}, \quad (2)$$

where S is the specific surface area of the open pores, and t is the thickness of the walls adjacent to this surface (having it). All the assumptions made in the definitions of S and t apply to V_w . We accept S_{BET} and $t = a_o - D_p$, so

$$V_w = S_{\text{BET}}(a_o - D_p). \quad (2a)$$

The apparent wall density $\rho_w = 1/V_w$ can be compared with the skeleton material density ρ_{sk} , and the reliability of the value of V_w (ρ_w) can be estimated. For example, for silica, $V_{sk} = 1/\rho_{\text{SiO}_2} = (1/2.2 \text{ g/cm}^3) = 0.454 \text{ cm}^3/\text{g}$. V_w also allows us to offer the dimensionless $Y = V_w/V_p$ as a generalized structural parameter OMM.

The volume of intra-wall pores, that is, closed and inaccessible pores (empty space) inside the walls $V_{iw} = (V_w - V_{sk})$, gives additional information about wall transformations. Since both open and closed intrawall pores are formed from the same material, the type of correlation between V_{iw} and V_p demonstrates features of the formation of the material.

5 Discussion. New insight on some published results

The suggested in current and previous works [1, 2] parameters (X , L_s , L_v , L_s/L_v , V_w , V_{iw} , V_w/V_p and t/D_p) were added to original ones (a_o , S_{BET} , V_p , D_p , and t) of some published investigations and new insight on the materials properties and new dependencies were obtained.

5.1 The pioneering work of Zhao et al. [19], which reported on the synthesis conditions of a series of 11 samples of an ordered mesoporous thick-walled silica SBA-15, has become classic. They used triblock copolymers: poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) ($\text{EO}_n\text{--PO}_m\text{--EO}_n$)—with different block lengths n and m as structural formers.

The independent variables were: $x_1 = n$ in EO_n , $x_2 = m$ in PO_m , x_3 —reaction temperature (35, 40 and 60 °C), x_4 —post-synthesis heating temperature (80, 90 and 100 °C) and x_5 —time of this heating (24 or 48 h). All samples were calcined at a temperature of 500 °C. The large wall thickness ensured good thermal stability of all samples. Our calculations and dependencies are given in ESM-3. The route number includes all the preparation conditions, that is, it corresponds to some generalized variable X .

5.1.1. The mutual and selective influence of process variables on parameters ESM-3 Table 1-1 (Table 1 in [19]) shows that changes in all structural parameters do not correlate with the run numbers. To simplify the pattern of S_{BET} , V_p , D_p and V_{iw} dependencies on the run numbers, we choose runs ## 2–6 with the same polymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ and a reaction temperature of 35 °C (i.e. with constant X_1 , x_2 , x_3), but differ only with temperature (x_4) and heating time (x_5) after synthesis. The following Table 2 shows that the growth of the combined (x_4 – x_5) variable (runs ## 2–6) leads to a smooth increase in D_p , but the smoothness $V_{iw} = f(\text{run \#})$ is broken (bold and italics) in run No. 4. And this happens not only with the new V_{iw} parameter, but also with the well-known S_{BET} and V_p in run No. 5 (ESM-3, Figs. 1-1, 1-2 and 1-3).

Table 2 Effect of post-synthesis heating (PSH) temperature and time on the structural parameters of SBA-15 (S_{BET} , D_p , V_p from Zhao et al. [19] + our V_{iw}), with permission from AAAS, 2019

Run #	x_4 – PSH temperature (°C)	x_5 – PSH time (h)	D_p (nm)	V_{iw} (cm ³ /g)	S_{BET} (m ² /g)	V_p (cm ³ /g)
2	None	None	4.7	3.96	690	0.56
3	80	24	6.0	3.68	780	0.80
4	80	48	7.7	2.66	820	1.03
5	90	24	8.5	2.86	920	1.23
6	100	24	8.9	2.18	850	1.17

It can be assumed that the deviations of S_{BET} , V_p in run 5 and V_{iw} in run 4 are the result of the mutual influence of all variables, including the constants x_1 – x_3 plus calcination. Note that the growth of S_{BET} , V_p and D_p leads to a decrease in V_{iw} , that is, to a contraction of the walls. Note also the selective effect of variables x_4 and x_5 on structural properties: on going from route 3 to route 4 V_{iw} falls due to an increase in the post-synthesis heating time from 24 to 48 h; in course of transition from route no. 3 to route no. 5, S_{BET} and V_p increase due to an increase in the post-synthesis heating temperature from 80 to 90 °C.

5.1.2. Sorting data Having constructed the data in the order of increasing D_p , we see that the maximum diameter value is obtained with a short length EOn ($n=5$), a low synthesis temperature (35 °C) and without post-synthesis heating (route #2). The highest S_{BET} , V_p , D_p , and t values were obtained for different routes (selective influence of variables). Thus, the choice of preparing conditions (variable X) depends on the process in which the material will be used, i.e. what is the parameter of interest. The values of $D_p=6$ nm were obtained in two equivalent runs 3 and 9. Runs 7 and 11 are equivalent for $\rho_w=0.28$ g/cm³.

5.1.3 The apparent density of the walls of the samples ρ_w is in the range of 0.23–0.45 g/cm³ (ESM-3, Table 2-1). Since the skeletal density of the silica walls is $\rho_{\text{sk}}=2.2$ g/cm³, one can say that we are dealing with hollow wall samples. The share of in-wall inaccessible empty space (V_{iw}/V_w) is from 80 to 90%, its standard deviation (STD) is only 3.9% (ESM-3, Table 1, 2). This is probably the case when the openwork architecture of the racks, which is formed inside the porous walls, ensures the strength of these walls [1]. The apparent volume of the walls V_w allows us to estimate the total specific volume of $V_o=V_p+V_w$, that is, the total volume of open pores and walls in 1 g of material. V_o depends on the pore diameter: increasing the pore diameter, we decrease the V_o (ESM-3, Fig. 2.1). And this is due to a decrease in V_{iw} intra-wall porosity, which demonstrates a similar to V_o , but less scattered dependence on D_p (Fig. 1).

5.1.4 The generalized structural parameter V_w/V_p as a stability parameter behaves like a wall thickness t ; both are inversely proportional to V_p ; both $t=f(V_p)$ and $V_w/V_p=f(V_p)$ dependences show a good correlation at $V_p=0.5$ – 0.8 cm³/g and a noticeable scatter at $V_p=1.0$ – 1.3 cm³/g, (ESM-3, рис. 1–7). The parameter (V_w/V_p) with $\text{STD}=52.7\%$ is more sensitive than the wall thickness t , for which $\text{STD}=30.5\%$.

5.1.5. Size effect The ratio t/D_p and the ratio of intrawall space V_{iw}/V_w are related, as shown in Fig. 2.

Fig. 1 Dependence of the volume of intra-wall pores V_{iw} on the diameter of open pores D_p (based on data Zhao et al. [19], with permission from AAAS 2019)

Fig. 2 Size effect on intra-wall porosity: V_{iw}/V_w dependence on t/D_p (based on Zhao et al. data from [19], with permission from AAAS, 2019)

This connection can be explained by the fact that OMM walls are built of porous solids. The surface of the wall has many peaks of roughness of different heights and distances between them. The molecules of the probing medium enter the different depths of the depressions between the peaks and close the openings so that the narrow, deep part of the cavities belongs to the V_{iw} . A set of peaks can be modeled with a set of perforated cylindrical sieves; the size of the sieve holes decreases from the center of the mesopores to the periphery, creating a set of molecular sieves similar to a device for separating particles. The diameter D_p obtained from the H_2 adsorption–desorption test, for example, DNLDFT, is the diameter of a conventional cylindrical sieve with openings smaller than the kinetic diameter of nitrogen molecules,

i.e. impermeable to N_2 molecules and larger, but permeable to smaller ones (for example, He); all that is not an adsorbate is an adsorbent, and D_p is the model boundary between V_p and V_w . Micropores are on one side of the surface and belong to the open pores volume V_p , while their submicroporous elongations (hereinafter referred to as intrawall pores), inaccessible to the adsorbate, are inside the walls and belong to the inner space V_{iw} . From Fig. 2 it follows that V_{iw}/V_w greater than 87%, correlate with t/D_p , that is, they are cracks caused by stress.

5.1.6. Pore lengths The order of L_v and L_s is $(1-6)E+10$ m. All values of the roughness coefficient $L_s/L_v > 1$ (from 1.01 to 1.62), that is, all samples have a wavy surface; One of the samples (run No. 8: $EO_{20}PO_{30}EO_{20}$, reaction temperature 60 °C, without heating after synthesis) has smooth walls ($L_s/L_v = 1.01$). This sample has the largest specific pore volume ($1.26 \text{ cm}^3/\text{g}$), the second largest surface ($1200 \text{ m}^2/\text{g}$), one of the smallest pore diameters (5.1 nm), but one of the largest pore lengths ($L_s = 62,000,000 \text{ km/g}$). The growth of V_{iw} leads to an increase in both L_s and L_v , but these correlations exist only in the region of low t/D values; high t/D (size effect) destroys it (ESM-3, Figs. 5.2 and 4.1).

5.1.7. Wall thicknesses The range of wall thickness was 3.2–7.3 nm. A good direct correlation exists between the wall thickness t and the specific length of the adsorbent layer L_v . It has even smaller scatter than $t = f(V_p)$ (ESM-3, Figs. 5.7, 3-4).

5.2 Klimova et al. [15] prepared samples of SBA-15 using only $EO_{20}PO_{70}EO_{20}$ triblock copolymer and varying 3 factors: x_1 —synthesis temperature (35 and 60 °C), x_2 —aging temperature (60 and 80 °C) and x_3 —aging time (24 and 48 h); a total of 8 experiments. All our calculations and dependencies are collected in ESM-2.

5.2.1. V_{iw} versus t/D_p Among other parameters (see above), Klimova et al. [15] measured the surface of micropores S_{mi} . Both S_{mi} versus t/D_p and V_{iw} versus t/D_p correlations are shown in ESM-2 (Figs. 2.1 and 2.2) and reflect the involvement of mechanical stress in the formation of both open micropores and intra-wall pores.

5.2.2. V_{iw} versus V_p Since both open and closed intra-wall pores are formed from the same reaction mixture, the dependence of V_p on V_{iw} demonstrates a peculiarity of material formation. Figure 3 shows the dependence of V_{iw} on V_p , confirming that the formation of the structure of the material can go in different ways.

If we take experiments with a constant synthesis temperature of 35 °C, the smoothness of dependencies will

Fig. 3 V_{iw} versus V_p . Two points (runs #3 and 7) separate from almost linear dependence $V_{iw} = f(V_p)$. Based on data [15] with permission Elsevier Inc

be disturbed in experiment no. 3 (ESM-2, Fig. 2.4); if we take experiments with a constant temperature of 60 °C, the deviation will occur in experiment no. 7 (ESM-2, Fig. 2.5). This once again confirms the idea of the mutual influence of processing variables.

5.2.3 STD of V_w/V_p . Standard deviations of V_w/V_p and t are 25.7% and 11.8%, respectively, therefore V_w/V_p is more sensitive to synthesis conditions.

5.2.4. L_s/L_v values The roughness factor of samples L_s/L_v varies from 1.16 to 1.42. The smallest value (the smoothest walls) has the SBA-15-8 sample, which has the maximum S_{BET} , V_p , D_p values and the minimum V_{iw} . This sample was obtained at a low synthesis temperature, a high aging temperature, and a short aging time.

5.2.5. S_{mi} and L_s/L_v The absence of a correlation between S_{mi} and L_s/L_v (ESM-2, Fig. 2.9) confirms the model [16].

5.3 Wall thickness OMM t is often considered as an indicator of their mechanical stability. V_{iw} and L_s can help to see the details of its changes. Cassiers et al. [3] studied the structural parameters (α_o , S_{BET} , D_p and V_p) of the wide range OMM (variable x_1 : MCM-41-T, MSM-41-FS, MCM-48-T, MCM-48-FS, HMS, KIT -1 and SBA-15) after mechanical compression of powders under pressure $P = 296 \text{ MPa}$ (variable x_2 : 0 and 296 MPa). Compression had a very small impact on α_o and D_p , but it significantly reduces S_{BET} and V_p (ESM-4).

5.3.1. V_p dependencies The figure of the dependence of V_p on D_p for all mentioned OMM, pressed and non-pressed,

shows that, despite the almost constant pore diameter D_p , the pore volume V_p changes 3 times (ESM-4, Fig. 1). To explain the reason for this change, let us test its dependence on the pore length L_s (ESM-4, Fig. 2). A good correlation of L_s with V_p suggests that the length (axial pore size) is the best linear characteristic of these samples.

5.3.2. Parameters changes The change Δ of any parameter was calculated as a relative value (%): $100 \cdot (\text{value after compression at } P = 296 \text{ MPa (index p) minus the value before compression, i.e. at } P = 0 \text{ (index o)}) / \text{value before compression}$, for example, $\Delta t (\%) = 100(t_p - t_o)/t_o$ (Table 3).

It can be seen that the effect of pressure on t depends on the type of OMM, but not on the initial wall thickness: for MCM-41-T and MSM-41-FS t did not change ($\Delta t = 0$), for MCM-48-T and HMS it decreased and for MCM-48-FS, KIT-1 and SBA-15 increased. The Δt values were almost unchanged, while the $\Delta(V_w/V_p)$ values increased markedly, confirming that the structural parameter V_w/V_p is more sensitive to compression than t .

5.3.2. Δt changes For all OMM studied, compression resulted in a decrease in both lengths of L_v and L_s and an increase in the coefficient L_s/L_v (ESM-4); if the surface was tortuous when unpressed, it became more tortuous (SBA-15); if the surface was fragmented, it became less fragmented (all other OOMs). A decrease in L_s should lead to a thickening of the wall, but the disappearance of a portion of the inner pores of V_{iw} works in the opposite direction, so that Δt can be negative, positive or zero.

5.3.3. SBA-15 behavior Of particular interest to us is the behavior of the SBA-15 sample (Table 3), since it can be compared with the SBA-15 sample from Hartmann and Vinu [7]. Table 4 shows the original [3] parameters of the SBA-15 sample, as well as calculated by us the apparent volume of walls V_w , the volume of intrawall pores V_{iw} , the lengths of the adsorbate volume L_v and the surface of the adsorbent L_s and some Δ -s.

Compressing the powder leads to the extrusion of air from the open pores in the volume ΔV_p ($0.48 - 0.63 = -0.15 \text{ cm}^3/\text{g}$) and to the reduction of intra-wall empty space ΔV_{iw} ($1.88 - 2.04 = -0.16 \text{ cm}^3/\text{g}$). The displaced air exits along the walls of the matrix in the amount of $\Delta V_{esc} = -0.15 + (-0.16) = -0.31 \text{ cm}^3/\text{g}$.

Unlike [3], Hartmann and Vinu [7] investigated the change of parameters of only one material, SBA-15, but by gradually increasing the external pressure P (by preparing granules at $P = 52, 130$ and 260 MPa) (Table 5). The a_o values and the N_2 adsorption parameters (S_{BET} , V_p , and D_p) decreased, and the wall thickness t increased. The apparent volume of the walls V_w and its hollow part V_{iw} grow to a pressure of 130 MPa , but then the growth stops. Perhaps, if the pressure were increased to 296 MPa , as in [3], further these volumes would decrease. The differences ΔV_p and ΔV_{iw} between pressed and non-pressed samples are also listed in the table.

For example, at $P = 260 \text{ MPa}$, the open pore volume V_p decreases from 1.61 to $0.96 \text{ cm}^3/\text{g}$ and the decrease is $\Delta V_p = 1.61 - 0.96 = 0.65 \text{ cm}^3/\text{g}$. In contrast to V_p , the inside wall space increases by $\Delta V_{iw} = 1.65 - 1.46 = 0.19 \text{ cm}^3/\text{g}$, which is less than ΔV_p by $0.65 - 0.19 = 0.46 \text{ cm}^3/\text{g}$. Thus, during pressing one part of the air ΔV_{iw} falls into the intra-wall space, and the second $\Delta V_{esc} = 0.46 \text{ cm}^3/\text{g}$ leaves along the walls of the matrix.

The behavior of the V_{iw} during the compression of this sample SBA-15 is fundamentally different from the behavior of the sample in Table 4: in the first case it increases, and in the second it decreases. Perhaps this is due to the initial wall thickness of the samples: under the action of mechanical pressure V_{iw} of the thick wall (3.95 nm [3]) decreases, and the thin wall -1.69 nm [7]—increases.

5.4 An interesting result was found through V_w , when we recounted Zhang et al. [20] data (ESM-5). The effect of post-synthesis steaming on the properties of a series of SBA-15 samples was investigated.

Table 3 Relative changes Δ of parameters of silicas after compression at 296 MPa (sorted by Δt as the key). Data [3] used with permission from CCC Inc. 2019

Sample	t_o (nm)	Δt (%)	$\Delta(V_w/V_p)$ (%)	ΔL_s (%)	$\Delta(L_s/L_v)$ (%)	ΔV_{iw} (%)
HSM	1.46	-13.7	42.6	-6.5	40.5	-45.1
MCM-48(T)	5.70	-1.2	47.5	-52.7	44.8	-57.9
MCM-41(T)	1.50	0.0	10.9	-24.1	10.9	-33.0
MCM-41(FS)	1.61	0.0	20.9	-27.6	18.6	-40.0
MCM-48(FS)	5.94	1.9	20.3	-26.1	12.9	-29.8
SBA-15	3.95	3.0	22.6	-5.3	13.9	-8.0
KIT-1	1.54	7.1	21.1	-13.1	11.8	-10.9

t —wall thickness, nm; t_o — t before pressure; V_w —wall apparent volume, cm^3/g ; V_p —specific pore volume, cm^3/g ; L_s —wall surface length, m/g ; V_{iw} —intrawall pores volume, cm^3/g

Table 4 Effect of tableting pressure P on SBA-15 parameters: original [3] (a_o , S_{BET} , V_p , D_p and t) and proposed in this article (V_w , V_{iw} , L_s , L_w , L_g , L_v) as well as the balance between a decrease in V_p (ΔV_p), V_w (ΔV_w) and the displaced gas volume ΔV_{esc} . According to [3] with the permission of CCC Inc. 2019

P, MPa	a_o (nm)	S_{BET} (m ² /g)	D_p (nm)	V_p (cm ³ /g)	t (nm)	V_w (cm ³ /g)	V_{iw} (cm ³ /g)	ΔV_p (cm ³ /g)	ΔV_{iw} (cm ³ /g)	ΔV_{esc} (cm ³ /g)	L_s^*1E-10 (m/g)	L_v^*1E-10 (m/g)	L_s/L_v
0	9.52	632	5.57	0.63	3.95	2.50	2.04	-	-	-	3.61	2.59	1.40
296	9.40	573	5.33	0.48	4.07	2.33	1.88	-0.15	-0.16	-0.31	3.42	2.15	1.59

Table 5 Effect of pelletizing pressure P on structural parameters (S_{BET} , V_p and D_p) SBA-15 [7] and calculated by us: the apparent volume of the walls V_w , the pore volume V_{iw} inside the wall and the balance between the increase V_{iw} (ΔV_{iw}), decrease V_p (ΔV_p) and the amount of outgoing gas ΔV_{esc} . Used data [7] with the permission of CCC Inc. 2019

P (MPa)	a_o (nm)	S_{BET} (m ² /g)	D_p (nm)	V_p (cm ³ /g)	t (nm)	V_w (cm ³ /g)	V_{iw} (cm ³ /g)	ΔV_p (cm ³ /g)	ΔV_{iw} (cm ³ /g)	ΔV_{esc} (cm ³ /g)	L_s^*1E-10 (m)	L_v^*1E-10 (m)	L_s/L_v
0	10.89	1130	9.2	1.61	1.69	1.91	1.46	-	-	-	3.91	2.42	1.61
52	10.52	1020	8.6	1.40	1.92	1.96	1.50	-0.21	0.05	-0.16	3.53	2.11	1.67
130	10.42	950	8.2	1.20	2.22	2.11	1.66	-0.41	0.20	-0.21	3.52	2.07	1.70
260	10.39	880	8.0	0.96	2.39	2.10	1.65	-0.65	0.19	-0.46	3.42	1.82	1.88

5.4.1. Samples S-3 and S-2 behavior Among the freshly prepared samples there is a sample S-3, synthesized at 120 °C. The density of its walls, calculated by us, was very high (1.61 g/cm³) and the skeletal volume fraction V_{sk} of the apparent volume of walls V_w was 73.3%. After steaming the samples, the apparent density of the walls of other samples increased, while the density of S-3 (3 h) became lower (1.21 g/cm³), and its V_{sk}/V_w decreased from 73.3 to 55.0%. Obviously, silica is rehydrated. Sample S-2, synthesized at 70 °C, also exhibits an interesting behavior: steaming for 3 h resulted in a twofold decrease in both V_p and V_w , so the V_w/V_p parameter did not change, but inside the walls the fraction of the skeleton volume (V_{sk}/V_w) has doubled.

5.4.2. Size effect The data of this work also include the volumes of micropores V_m (range 0.001–0.05 cm³/g). A function V_m versus t/D_p (ESM-5, Fig. 1) showed that small values $V_m < 0.1$ cm³/g do not correlate with t/D_p , whereas $V_m > 0.1$ cm³/g correlates well with him. One can say that small V_m were obtained from the “crown” of the forming polymer [11], but large V_m are cracks caused by mechanical stresses. The points of dependence of V_{iw}/V_w on t/V_p (ESM-5, Fig. 2-2) are strongly scattered, but they retain the tendency of direct proportion.

5.4.3. Steaming effect Steaming causes a decrease in pore diameter, volume and surface. After steaming, different samples have the highest S_{BET} , V_p , D_p , t and V_{iw}/V_w values, namely S-1 (3 h), S-3 (3 h), S-3 (3 h), S-1 (24 h) and S-2 (3 h). Thus, the choice of sample depends on our property of interest.

5.4.4. Steaming and roughness factor Steaming causes surface fragmentation ($L_s/L_v < 1$).

5.5 Thielemann et al. [21] studied the effect of washing freshly prepared SBA-15 with water, ethanol, and their mixtures on the properties of SBA-15. The question arises—does this rinse open up the passages into the intrawall pores inaccessible to nitrogen before rinsing.

5.5.1. V_{iw} change The calculated V_w and V_{iw} of two samples (1B and 2C), washed with a mixture of ethanol and ethanol–water, are reduced to 20–30%; It is obvious that ethanol blurs the mouths of previously inaccessible intrawall pores and converts part of the internal pores into open micropores, so that both the surface of the micropores and the total surface of the pores increase.

5.5.2. Roughness constancy After washing with ethanol, SBA-15 is compressed: both S_{BET} and V_p are reduced. L_v and

L_s also decreased; however, they decreased equally, so the roughness did not change.

5.6 Lee et al. [22] prepared a series of 7 samples of ordered mesoporous carbon synthesized inside a solid matrix of mesoporous silica (MSU-H); the latter was then removed. Sucrose was used as a carbon precursor, and boric acid (BA) was added to sucrose as an agent that widens the pores. BA (0 to 25%) was the only processing variable. With an increase in the BA content from 0 to 25 wt% the apparent volume of the walls V_w decreased 10 times: from 10.56 to 1.01 cm³/g (ρ_w increased from 0.09 to 0.98 g/cm³). Low density values are typical for foams, so it can be assumed that the BA in this work is a defoamer. As BA% increases, the roughness coefficient increases from 0.79 to 1.78, so a smooth surface ($L_s/L_v = 1$) can be obtained with BA < 2%.

5.6.1. Size effect The intrawall pore volume V_{iw} was calculated based on a skeletal amorphous carbon density of 2.0 g/cm³. V_{iw} is caused exclusively by stress (Fig. 4).

5.6.2. BA effect Violation of smooth dependences of V_p , S_{BET} and V_{iw} on BA was observed at BA = 16%.

5.7 The Co-SBA-15 series was obtained by Lou et al. [17] by direct synthesis; the pH of the reaction mixture (0.0–7.0) and Co/Si (0.02–0.236 mol. %) were two variables. By simultaneously increasing the pH and Co content, the authors gradually increased the density of the walls from 0.25 to 1.47 g/cm³, that is, from the structure of the foam to the dense walls. The roughness factor L_s/L_v changed from 0.87 to 0.42, i.e. the surface has become more fragmented.

Fig. 4 The dependence of the pore volume inside the wall V_{iw} cm³/g, on the ratio of wall thickness t to the average pore diameter D_p (size effect [2]). Data Lee et al. [21] were used, with permission from Wiley–VCH Verlag GmbH & Co. KGaA 2019

5.8 The model mentioned above [16, p. 183], which distinguishes microporosity from surface roughness, was verified by adding L_s/L_v to the data Zukerman, Titelman et al. [23] to track changes in microporosity and roughness. Two samples of SBA-15 were prepared according to the classical technology, but with different hydrothermal synthesis times: 1 day (SBA-15-HM) and 3 days (SBA-15-LM). These samples had a micropore surface area 37.6% and 18.8% of the total, respectively, and L_s/L_v ratios of 1.56 and 1.25, respectively. Consequently, an increase in the duration of the synthesis reduces both the surface of the micropores and the roughness, healing the walls of SBA-15. Then the samples were used as the hosts for the precipitation of TiO_2 . The TiO_2 content was varied from 8 to 50 wt.% for both samples. In the SBA-15-HM sample, the percentage of micropores decreased from 37.6 to 11.6%, but L_s/L_v remained almost constant (≈ 1.5). Sample SBA-15-LM repeated the picture: the surface of micropores changed from 18.8 to 4.4%, but L_s/L_v did not change. Therefore, the filling of the SiO_2 micropores by TiO_2 did not affect the surface roughness, which is consistent with [16].

5.9 Another type of roughness was introduced by Smith et al. [24]. The wide distribution of micropores was taken as the cause of surface roughness and is designated as the fractal surface size (SFD).

In the experiments, they controlled the SBA-15 roughness by the calcination temperature after synthesis. Table 6 shows a fragment of their data and our calculations of L_s/L_v based on their data.

The relative values of L_s/L_v and SFD show that the contribution of SFD to L_s/L_v is small, which speaks in favor of the model [16].

5.10 Landau, Titelman et al. [25] prepared three catalysts based on sulfated zirconia (SZ): the first was prepared by precipitating Zr hydroxide from ZrOCl_2 followed by sulfuric acid (SZ-Ref), the second by a similar procedure using ZrOCl_2 with a block copolymer of P123 (NS-SZ). In addition, in the third sample SZ was deposited inside SBA-15 (SZ/SBA). Samples varied greatly in all characteristics, including ZrO_2 crystal size, surface area, pore volume, pore diameter, and S/Zr ratio. Calculations of L_s and L_v (Table 7) give two results: (1) $L_s/L_v \approx 1$ for all samples, which indicates that

Table 7 Total pore length L_v , L_s and roughness factor L_s/L_v calculated according to [25]

Sample	L_v *E-9, m	L_s *E-9, m	L_s/L_v
SZ-Ref	8.8	8.6	0.98
NS-SZ	8.1	8.0	0.99
SZ/SBA	24.6	24.8	1.01

the smoothness of the pore surface is due to SZ, and (2) a large difference (three times) in the pore length between SZ/SBA and other catalysts are provided with an ordered SBA structure.

6 Conclusions

In continuation of the previous works [1,2], the concept of *equivalent* generalized technological variables (technological routes) was proposed, based on the mutual influence of process variables and allowing to choose the most economical conditions for preparing materials. *Sorting* data by the property of interest as a key allows to modify the table so that the experiments are arranged in order of increasing (decreasing) of the force of the impact of variables on this property; in addition, equivalent routes are nearby.

For porous materials, two specific pore lengths have been proposed: the adsorbate volume length L_v and the adsorbent surface length L_s ; lengths were used to derive an *equation* relating the hydraulic pore diameter D_h to the average D_p : $D_p = D_h(L_s/L_v)$, where the classical $D_h = (4V_p/S_{\text{BET}})$ is the pore diameter with smooth walls, and (L_s/L_v) is a type of roughness factor. Examples of smooth-walled samples are given. The roughness factor is generalized structural parameter of any porous material.

For ordered mesoporous materials (OMM), the formula for the apparent volume of walls is suggested $V_w = S_{\text{BET}} \cdot t$. The generalized variable $Y = V_w/V_p$ is a more sensitive indicator of the structural stability of OMM than the wall thickness t . V_w allows to estimate the total specific volume of OMM V_o and the inner walls pore volume V_{iw} . The dependence of the pore volume inside the walls V_{iw} on open pores volume V_p confirms the idea of the mutual influence of processing variables.

Table 6 Two types of roughness: fractal surface size (SFD) [24] and our L_s/L_v . Influence of calcination temperature on the structural properties of SBA-15 (S_{BET} , V_p , D_p), (SFD) [24] and L_s/L_v

Calcination temperature (C)	S_{BET} (m ² /g)	V_p (cm ³ /g)	D_p (nm)	SFD	L_s *E-10 (m)	L_s/L_v	Relative SFD	L_s/L_v
500	887	0.86	8.1	2.40	3.49	2.09	1	1
700	705	0.71	7.7	2.35	2.92	1.91	0.98	0.92
850	438	0.50	6.8	2.20	2.05	1.49	0.92	0.71

The existence of a stress-induced mechanism of formation V_{iw} ($V_{iw} = f(t/D_p)$) was discovered.

The parameters proposed in [1, 2] and the present work do not require any additional test methods; at the same time, they significantly expand information about the features of the formation and properties of porous materials.

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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