Mechanical Characterization of Hierarchical Structured Porous Silica by in Situ Dilatometry Measurements during Gas Adsorption

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ABSTRACT: Mechanical properties of hierarchically structured nanoporous materials are determined by the solid phase stiffness and the pore network morphology. We analyze the mechanical stiffness of hierarchically structured silica monoliths synthesized via a sol−gel process, which possess a macroporous scaffold built of interconnected struts with hexagonally ordered cylindrical mesopores. We consider samples with and without microporosity within the mesopore walls and analyze them on the macroscopic level as well as on the microscopic level of the mesopores. Untreated as-prepared samples still containing some organic components and their calcined counterparts of varying microporosity are investigated. To determine Young’s moduli on the level of the macroscopic monoliths, we apply ultrasonic run time measurements, while Young’s moduli of the mesopore walls are obtained by analysis of the in situ strain isotherms during N₂ adsorption at 77 K. For the latter, we extended our previously reported theoretical approach for this type of materials by incorporating the micropore effects, which are clearly not negligible in the calcined and most of the sintered samples. The comparison of the macro- and microscopic Young’s moduli reveals that both properties follow essentially the same trends, that is, calcination and sintering increase the mechanical stiffness on both levels. Consequently, stiffening of the monolithic samples can be primarily attributed to stiffening of the backbone material which is consistent with the fact that the morphology on the mesopore level is mainly preserved with the post-treatments applied.

1. INTRODUCTION

Recently, adsorption-induced deformation found increasing interest from both experimental and theoretical point of view. When fluids adsorb on a solid surface, the interatomic forces of solid−fluid interactions cause noticeable stresses. For nanoporous materials, having high surface area, these stresses result in noticeable strains. This is what is referred to as adsorption-induced deformation, which is often seen as an undesired phenomenon. For example, adsorption-induced deformation of coal during enhanced coal-bed methane extraction complicates the process. Furthermore, strains induced by adsorption alter the molecular transport in zeolite membranes. On the other hand, adsorption-induced deformation is a promising tool for developing sensors and actuators, as well as for characterization of porous materials, because the strains are very sensitive to the pore sizes.

A quantitative understanding of the basic physical mechanisms of this phenomenon on the level of individual micro-/mesopores has been elaborated based on atomistic modeling as well as on analytical approaches. Yet, it is very difficult to predict macroscopic stiffness parameters from the analysis of adsorption-induced deformation data because most of the porous systems used in applications have complex geometries thus strongly influencing the resulting macroscopic mechanical properties. Moreover, also the physical interactions on the local level strongly depend on the pore size and morphology, resulting in significantly different deformation behaviors of micro- and mesoporous materials.
A pivotal work with respect to mesopore deformation in disordered porous solids was published by Scherer in 1986, providing a detailed analysis of adsorption-induced deformation of Vycor porous glass by using an appropriate microstructural mechanical model for the disordered pore geometry. Scherer’s work showed in particular that the elastic moduli of Vycor are noticeably lower than the values for a common silica glass, unless the sample is calcined at the temperature above 800 °C.

The availability of mesoporous materials with monodisperse pore morphologies, such as the almost perfect cylindrical pores in MCM-41 and SBA-15 types of materials, made the analysis of adsorption-induced stresses and strains easier. Simple mechanical models have been proposed to obtain macroscopic stiffness parameters from such data. Recently, we presented a systematic analysis of the adsorption-induced deformation of porous materials with cylindrical mesopores by analytically calculating both the axial and the radial stresses acting on the pore walls. A simple, yet powerful mechanical model based on the Derjaguin–Broekhoff–de Boer (DBdB) theory of capillary condensation allowed the analytical calculation of the axial macroscopic stiffness parameters from such data. In parallel, a rigorous analytical thermodynamic treatment of adsorption-induced deformation of cylindrical mesopores was developed. Recently, we presented a systematic analysis of the adsorption-induced deformation of porous materials with cylindrical mesopores by analytically calculating both the axial and the radial stresses acting on the pore walls. A simple, yet powerful mechanical model based on the Derjaguin–Broekhoff–de Boer (DBdB) theory of capillary condensation allowed the analytical calculation of the axial and radial strains and comparing them to experimental data. Here, we advance this analytical approach on adsorption-induced stress and strain to study the impact of post-treatments on the mechanical stiffness of hierarchically structured porous silica. The goal of this work is to compare mechanical properties of the mesopore walls derived from in situ dilatometry via modeling of the strain isotherm with independent mechanical measurements on the macroscopic scale of the material. From the N2 adsorption isotherms, we obtained the combined micro- and mesopore volume Vgurich with the Gurvich rule as well as the specific micropore volume Vmic and the external surface area Sext by the t-plot method using the reference isotherm for sintered silica given in ref 37. From these quantities, we calculated the samples’ average mesopore diameter dmeso = 4Vmeso/(Vmic + 1/|p|), the mesoporosity of the struts ϕmeso = Vmeso/(Vmic + Vmic + 1/|p|), and the macroporosity of the strut network ϕmac = (1/|p| − Vmic)−1/|p|. Here, Vmic = Vgurich − Vmic is the material’s specific mesopore volume, and ρbulk is the density of the nonporous skeleton as determined by He-pycnometry taken from ref 44 for the untreated sample (ρbulk = 1.76 g/cm³) and from ref 45 for all other samples consisting of pure silica (ρbulk = 2.2 g/cm³).

For mechanical characterization of the model materials, we applied a self-built ultrasonic runtime setup, which determines the material’s longitudinal sound velocity vmin from the length of the sample and the runtime of an ultrasonic pulse. The sound velocity is directly correlated with the material’s Young’s modulus Emicropole = (1 − νp − 2νs)/(1 − 2νs)p sound⁴,⁴⁹ where the Poisson ratio ν of the monolithic sample was assumed to be 0.2 according to refs. 7,40.

2.3. N2 Adsorption with in Situ Dilatometry. N2 adsorption measurements at 77 K with in situ dilatometry were performed the same way as in our previous study. In short, the experimental setup consists of a commercial volumetric sorption instrument (ASAP 2010 by Micromeritics) and a self-built sample holder containing a dilatometer. A schematic of the dilatometer is shown in ref 16. The overall setup determines the common specific adsorption isotherm N2(p/p0)/m describing the molar amount adsorbed N2 per sample mass m as a function of the relative gas pressure p/p0. In addition, the setup yields the sample’s strain isotherm εy(p/p0), that is, the relative length change of the monolithic sample again as a function of p/p0. The accuracy of the strain is approximately 10⁻⁴ for a typical sample length of 2 cm. The adsorption measurements followed common procedures: we used N2 of purity 5.0 as adsorptive and applied liquid N2 to maintain the temperature of the sample at 77 K. The saturation pressure of N2 was measured at regular intervals during the experiment. Prior to the measurement, the samples were degassed inside the sample holder for 1 d at 110 °C and pressures below 10⁻⁵ mbar.

2.4. Models of Adsorption-Induced Deformation. In this section we summarize the theoretical models applied to analyze the strain isotherms of the model materials. As will be shown in the following, the model materials can be grouped into (i) meso/macroporous samples, whose strain isotherm was shown to be well described by the cylindrical mesopore-based model and (ii) samples that additionally include micropores within their mesopore walls. For the latter, the mesopore model has to be complemented by a model for micropore deformation. Here, we employ an empirical approach...
based on the Langmuir adsorption model suggested by Neimark et al.,\textsuperscript{38} combined with the structural model previously applied to microporous carbons.\textsuperscript{16} Because both the meso- and micropore models imply the assumption of liquid-like adsorbate properties, all adsorption isotherms are given in units of specific liquid volume, that is, $N_c(p/p_0)/mV_t$ with $V_t$ the molar volume of the liquid adsorbate.

2.5. Meso–Macroporous Hierarchical Structured Silica. The treatment of the experimental data is based on the model for adsorption-induced deformation presented in ref 37, which was specifically developed for meso–macroporous hierarchical-structured silica with cylindrical mesopores. Here, we present a short summary of the model directly relevant for data evaluation.

The major contribution to the adsorption-induced deformation of the hierarchical-structured porous silica arises from the adsorption-induced axial and radial stresses within the cylindrical mesopores of the material, whereas adsorption in macropores has little to no impact on the material’s strain and may be neglected. For the quantitative description, the model combines the DBdB theory for adsorption in cylindrical mesopores,\textsuperscript{49,50} the adsorption stress model introduced by Ravikovitch and Neimark,\textsuperscript{18} and the mechanical model of a cylindrical tube.\textsuperscript{37} Because the mesopores typically undergo capillary condensation during the adsorption process, their adsorption and consequently also their strain isotherms are separated into the adsorption film and filled pore regime, respectively. The adsorption isotherm is thus described by two equations containing the model parameters $S$, the specific mesopore surface area, and $R$, the mesopore radius

$$N_{\text{film}}(p/p_0)/mV = S\left(h(p/p_0) - h(p/p_0)^2/2R\right)$$  

$$R_gT\ln(p/p_0) = -V_L\left[\Pi(h) + \frac{\gamma_v}{R - h}\right]$$

Here, $h$ is the thickness of the concentric adsorbate film forming on the wall of the cylindrical mesopore, which in turn is determined by the condition of the thermodynamic equilibrium, eq 1b. $\Pi(h)$ is the disjoining pressure isotherm characterizing the adsorbate–adsorbent interaction in the film, and $\gamma_v$ is the liquid–vapor surface tension of the adsorptive. $R_g$ is the gas constant, and $T$ is the temperature. Following our previous work, we apply the empirical disjoining pressure isotherm derived for sintered silica.\textsuperscript{37} Because of the classical approximation of the DBdB theory, the volume adsorbed in the filled pore regime of the adsorption isotherm is constant and in the case of a cylindrical pore equal to the pore volume given by

$$N_{\text{filled}}(p/p_0)/mV = \frac{1}{2} S \cdot R$$

The transitions between the film and the filled pore regimes, that is, capillary condensation and capillary evaporation, occur at the film thicknesses $h_f$ and $h_s$, respectively, given by

$$\frac{d\Pi(h)}{dh} \bigg|_{h=h_f} = \frac{\gamma_v}{(R - h_f)^2} = 0$$

$$R_gT\ln(p/p_0) = -2V_L\left[\frac{\gamma_v}{R - h_s} + \frac{1}{(R - h_s)^2}\int_{h_s}^{h} (R - k')\Pi(k') \, dk'\right]$$

The film thicknesses $h_f$ and $h_s$ can be correlated with respective relative pressures $p_f/p_0$ and $p_s/p_0$ by eq 1b.

The stresses within the cylindrical mesopore are anisotropic with respect to the radial (normal to the pore wall) and axial (parallel to the pore wall) directions ($\sigma_{\parallel}$ and $\sigma_{\perp}$, respectively) and are determined by the following equations in the film and filled pore regimes\textsuperscript{37}

$$\sigma_{\parallel,\text{film}} = -\frac{R}{R} h\Pi(h) + \int_{h}^{h_0} k\Pi(k') \, dk' - \frac{1}{R - h}$$

$$\sigma_{\perp,\text{film}} = \frac{2R}{R}\frac{2}{\Pi_0}\int_{h_0}^{h} (R - h')\Pi(h') \, dh' - h\left(1 - \frac{1}{R - h}\right)$$

$$\sigma_{\parallel,\text{filled}} = -\frac{\gamma_v}{R} + p_f + \frac{R_gT}{V_L}\ln(p_f/p_0)$$

$$\sigma_{\perp,\text{filled}} = -\frac{2\gamma_v}{R} + p_f + \frac{R_gT}{V_L}\ln(p_f/p_0)$$

Here, $\gamma_v(h)$ is the (negative) change of the adsorbent’s surface energy because of the adsorption of gas molecules and $p_f$ is the saturation pressure of the adsorptive.

The dilatometric strain $\varepsilon_{\text{dil}}$ recorded on the macroscopic scale is modeled as a simple superposition of axial and radial strains of the cylindrical tube, that is, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, respectively. The model parameters are Young’s modulus of the mesopore wall $E_{\text{wall}}$ and a geometric parameter $x$

$$\varepsilon_{\text{dil}} = x\varepsilon_{\perp} + (1 - x)\varepsilon_{\parallel}$$

$$\varepsilon_{\parallel} = \frac{1}{E_{\text{wall}}} - \frac{\phi_{\text{meso}}}{x} (2\sigma_{\parallel} - \varepsilon_{\text{wall}}\sigma_{\parallel})$$

$$\varepsilon_{\perp} = \frac{1}{E_{\text{wall}}} - \frac{\phi_{\text{meso}}}{1 - x} (2\sigma_{\perp} - 2\varepsilon_{\text{wall}}\sigma_{\perp})$$

Here, $\phi_{\text{meso}}$ is the porosity of the mesoporous struts determined from adsorption data (see Section 2.2). Poisson’s ratio of the pore wall, $\nu_{\text{wall}}$, is not known but can be estimated to be in the range of 0.20 ± 0.05 for silica materials.\textsuperscript{51} The parameter $x$ is related to the geometrical aspect ratio of the struts forming the macropore network. More precisely, $x$ and $1 - x$ denote the relative contributions of axial and radial tube strain, respectively, to the effective macroscopic length change measured by dilatometry (see Figure 1d and ref 37).

2.6. Micropores. To include adsorption and strain related to the microporosity of the materials into the model described in the previous section, we use the Langmuir adsorption model for the isotherm

$$N_{\text{mic}}(p/p_0)/mV = N_{\text{mic}} - \frac{b - p/p_0}{1 + b - p/p_0}$$

including the parameters $V_{\text{mic}}$, the specific micropore volume of the material, and the parameter $b$ characterizing the adsorbate interaction with the micropores. To understand the physical meaning of the parameter $b$, we note that $1/b$ corresponds to the relative pressure where the micropore filling is 50% of its maximum volume.

Combining the Langmuir adsorption equation with the adsorption stress model,\textsuperscript{52} we obtain the stress within the micropore volume because of adsorption

$$\sigma_{\text{mic}}(p/p_0) = \frac{R_gT}{V_L}\ln(b - p/p_0 + 1) + \frac{\delta h}{\delta p_{\text{mic}}} b - p/p_0 + 1$$

Here, the parameter $\delta h/\delta p_{\text{mic}}$ describes the change of the adsorbate–micropore interaction because of the change of the micropore volume. Typically, $\delta h/\delta p_{\text{mic}}$ can be expected to be negative because the positive stress (and strain) of the microporous matrix increases the
average micropore size, reducing its solid–fluid interaction. This effect was analyzed earlier by phenomenological and atomistic models in various studies.24,39,52−55 Notably, the simplistic model described here assumes the stress within the micropores to be isotropic.

To quantify the strain of the microporous matrix $\varepsilon_{\text{wall}}$ resulting from $\sigma_{\text{mic}}$ in the wall of the cylindrical mesopores, we apply a simple model for volumetric strain originally proposed in ref 39 for microporous carbon

$$
\varepsilon_{\text{wall}}(p/p_0) = \frac{\phi_{\text{mic}}}{K_{\text{wall}}} \sigma_{\text{mic}}(p/p_0) = 3(1 - 2\nu_{\text{wall}}) \frac{\phi_{\text{mic}}}{E_{\text{wall}}} \sigma_{\text{mic}}(p/p_0)
$$

(10)

Here, $\phi_{\text{mic}}$ is the microporosity, and $K_{\text{wall}}$ is the effective bulk modulus of the mesopore walls. The parameter $\phi_{\text{mic}}$ may be determined from $N_2$ adsorption analysis (compare Section 2.2), whereas the parameter $K_{\text{wall}}$ may be expressed in terms of $E_{\text{wall}}$ and $\nu_{\text{wall}}$, which are the same parameters as used in eq 7a.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of Model Materials.

Figure 1 shows a photograph, as well as a SEM, and transmission electron microscopy (TEM) image of the hierarchically organized, monolithic silica. These images of the untreated reference sample exemplify the optical appearance and microstructural morphology of all sample investigated in this study because they all look very similar on the basis of these characterization techniques. In addition, a sketch of two struts is included in Figure 1d to visualize the geometrical origin of the parameter $x$ applied in eq 6.

Figures 2a and 3a show $N_2$ adsorption isotherms for the untreated sample and a macro-/meso-/microporous sample (Calc), respectively. The isotherms for the other three samples investigated in this work are presented in the Supporting Information (Figures S1−S3). The results of the evaluation of the $N_2$ sorption isotherms, that is, the specific Gurvich volume $V_{\text{Gurvich}}$, the specific micropore volume $V_{\text{mic}}$, the specific external surface area $S_{\text{ext}}$, and the average mesopore diameter $d_{\text{meso}}$ are summarized for all samples in Table 1. The bulk density $\rho$ of the degassed sample and He density $\rho_{\text{He}}$ are also given in Table 1, along with the parameters calculated from...
these values, that is, the microporosity of the mesopore walls $\phi_{\text{mic}}$, the mesoporosity of the struts $\phi_{\text{meso}}$, and macroporosity of the strut network $\phi_{\text{mac}}$ (see Section 2.2). From the sample characterization, the following major trends can be deduced: all samples exhibit N$_2$ adsorption isotherms typical for mesoporous materials with a narrow pore size distribution. Both the untreated sample and the sample sintered at 950 °C do not contain any measurable amount of micropores. The calcined sample and those sintered at 750 and 850 °C do exhibit a measurable amount of micropores within the mesopore walls. The microporosity of the mesopore walls is the highest for the calcined sample and decreases for increasing sintering temperature. With respect to the mesopore structure, we find that calcination increases both mesoporosity and average mesopore diameter. The increase of the mesopore diameter along with the presence of microporosity after calcination is interpreted as removal of the organic phase (most likely ethoxy surface groups and residual surfactant), which is expected to be located within the mesopore walls and on its surface. Sintering of the already calcined material decreases the mesoporosity in parallel to the microporosity. However, although the decrease of the microporosity appears as a rather continuous process, the decrease in mesoporosity exhibits a significant step between sintering at 850 and 950 °C. Noteworthy, the macroporosity of the strut network is approximately constant for all samples, indicating that the post-treatments of calcination and sintering affect primarily the meso- and micropore structures of the material.

Figures 2b and 3b show the N$_2$ strain isotherms for the samples Untreated and Calc, respectively, and Figures S1b–S3b show the strain isotherms for the three sintered samples. Except for very low pressures, all strain isotherms show characteristics similar to that already described in ref 37, that is, the strain continuously increases with increasing relative pressure, interrupted by a slight dip at the points of capillary condensation for adsorption and capillary evaporation for desorption, respectively. The magnitude of the strain at the maximum relative pressure appears to be largest for the untreated sample and becomes progressively smaller as the heat treatment temperature increases. Notably, the maximum strain of the sample Sint950 is by almost an order of magnitude smaller as compared to the sample Untreated.

Although the strain is always positive for the samples Untreated and Sint950, this is not the case for the other three samples. These three samples, containing all some amount of microporosity (see Table 1), exhibit clearly a negative strain at very low pressures as visualized in more detail in Figure 4 for the sample Calc and in Figures S4 and S5 for the samples Sint750 and Sint850, respectively. Such negative strains are well known for instance from microporous carbons and are related to the interplay between adsorption and confining effects. Therefore, the modeling of the strain isotherms for these three samples will need to take such micropore effects into account as will be done in Section 3.3.

![Figure 4](image_url). N$_2$ adsorption isotherm at 77 K (a) and corresponding strain isotherm (b) of the sample Calc on a logarithmic relative pressure scale. Full symbols denote experimental adsorption, open symbols denote experimental desorption data. The red solid line is the result of the theoretical modeling according to eq 1. The red dot in the theoretical strain isotherm marks the point of capillary condensation.

We also mention here that the strain desorption isotherm for the untreated sample in Figure 2b goes above the adsorption isotherm in the film regime. This is somewhat unexpected because the adsorption isotherm is fully reversible in this range of pressures (Figure 2a). Although we cannot offer a thorough explanation for this behavior, it should be noted that this effect is reproducible and characteristic for all untreated samples containing organic residues during N$_2$ adsorption at cryogenic temperatures and it is not observed for adsorption measurements at room temperatures.

### 3.2. Mechanical Analysis of Non-Microporous Model Materials
To model the experimental strain data of the samples investigated, we apply two different approaches: for the purely meso- and macroporous samples, we may directly follow the evaluation strategy reported in ref 37 utilizing eqs 1a–7a. For the samples containing also micropores, we refer to the next section.

From the modeling of the adsorption isotherms of the two macro-/mesoporous samples (samples Untreated and Sint950, see Figures 2a and S3a) by eqs 1a–3a, we obtain the parameters $S$ and $d = 2R$ (Table 2), which are in good agreement with the parameters $S_{\text{ext}}$ and $d_{\text{meso}}$ obtained by

| sample   | $\rho_{\text{tv}}$ [g/cm$^3$] | $\rho$ [g/cm$^3$] | $V_{\text{Griessi}}$ [cm$^3$/g] | $S_{\text{meso}}$ [m$^2$/g] | $V_{\text{mic}}$ [cm$^3$/g] | $d_{\text{meso}}$ [nm] | $V_{\text{mac}}$ [cm$^3$/g] | $\phi_{\text{mic}}$ [%] | $\phi_{\text{meso}}$ [%] | $\phi_{\text{mac}}$ [%] |
|----------|-----------------------------|------------------|---------------------------------|-----------------------------|-----------------------------|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Untreated| 1.76                        | 0.373            | 0.341                           | 250                         | 0                           | 5.4             | 1.77                         | 0                           | 37.5                        | 66.1                        |
| Calc     | 2.20                        | 0.348            | 0.622                           | 380                         | 0.10                        | 5.5             | 1.79                         | 18.0                        | 48.5                        | 62.5                        |
| Sint750  | 2.20                        | 0.383            | 0.452                           | 290                         | 0.04                        | 5.7             | 1.70                         | 8.1                         | 45.4                        | 65.3                        |
| Sint850  | 2.20                        | 0.423            | 0.387                           | 250                         | 0.03                        | 5.7             | 1.52                         | 5.8                         | 42.7                        | 64.4                        |
| Sint950  | 2.20                        | 0.525            | 0.239                           | 200                         | 0                           | 4.8             | 1.21                         | 0                           | 33.0                        | 63.9                        |
Table 2. Results of Modeling of Adsorption and Strain Isotherms as Well as Ultrasonic Runtime Measurements

| sample     | $S$ [m$^2$/g] | $d$ [nm] | $b$ | $\frac{\partial b}{\partial \epsilon_{\text{exp}}}$ | $x$ [-] | $E_{\text{wall}}$ [GPa] | $E_{\text{monolith}}$ [MPa] |
|------------|---------------|---------|-----|---------------------------------|--------|-----------------|------------------|
| Untreated  | 260           | 5.2     |     |                                 | 0.32   | 14              | 500              |
| Calc       | 350           | 6.0     | 9000|                                 | 0.32   | 27              | 1100             |
| Sint750    | 295           | 5.6     | 5000|                                 | 0.32   | 42              | 1920             |
| Sint850    | 255           | 5.6     | 2000|                                 | 0.32   | 56              | 2670             |
| Sint950    | 200           | 4.7     |     |                                 | 0.32   | 92              | 3065             |

For the discussion of our results, we compare now Young’s moduli obtained for the samples on the monolithic scale via ultrasonic runtime measurements ($E_{\text{monolith}}$) and the respective values determined for the moduli on the microscopic scale via the analysis of the strain isotherms, $E_{\text{wall}}$ (see Table 2). As a general remark, the relation between $E_{\text{wall}}$ and $E_{\text{monolith}}$ is complex because it depends on the structural parameters of the mesoporous strut and the macroporous strut network as well as the interconnections of the struts at their joints. Developing a quantitative relationship would require a detailed finite element analysis of a realistic 3D model of the macroporous network, which is a topic that is beyond the scope of the current paper. To get at least a qualitative estimate, we assume that the macroporous strut network can be described by the Gibson–Ashby model of quadratic modulus-density scaling of a random network, for the macropores and that Young’s modulus of an individual strut scales directly with its solid phase fraction ($1 - \phi_{\text{meso}}$). This approach leads to

$$E_{\text{monolith}} = (1 - \phi_{\text{mic}})^2(1 - \phi_{\text{meso}})E_{\text{wall}} \quad (11)$$

As can be seen from Figure 5 and the data presented in Table 2, the estimate according to eq 11 provides values for $E_{\text{wall}}$ which are about 2–3 times lower than the ones determined by the analysis of the in situ dilatometry data using eq 6. However, the factor between $E_{\text{monolith}}$ and the two sets of values for $E_{\text{wall}}$ is essentially identical, that is, the sample Sint950 exhibits a monolithic Young’s modulus approximately six times larger than that found for the sample Untreated, which is approximately the same factor found between the Young’s moduli of their mesopore walls determined by either approach. This leads to the conclusion that the increase of the monolithic Young’s modulus $E_{\text{monolith}}$ from sample Untreated to Sint950 is primarily the result of the increased Young’s modulus of the mesopore walls $E_{\text{wall}}$. With respect to eq 11, this result is reasonable because the porosities of the strut network $\phi_{\text{mic}}$ and the mesoporous struts $\phi_{\text{meso}}$ are comparable for both samples (Table 1).
superposition of the materials strain due to mesopore deformation (eq 7a) and strain due to micropore deformation (eq 10)

\[
\varepsilon_{\text{all}}(p/p_0) = \frac{1}{3} \varepsilon_{\text{wall}}(p/p_0) + (1-x)\varepsilon_{\text{mic}}(p/p_0) + x\varepsilon_{\text{meso}}(p/p_0)
\]

\[
\varepsilon_{\text{all}}(p/p_0) = (1 - 2\nu) \phi_{\text{mic}} E_{\text{wall}}^{-1} \sigma_{\text{mic}}(p/p_0)
\]

\[
\varepsilon_{\text{all}}(p/p_0) = (1 - 2\nu) \phi_{\text{meso}} E_{\text{wall}}^{-1} \sigma_{\text{meso}}(p/p_0) - 2\nu \sigma_{\text{mic}}(p/p_0)
\]

\[
\varepsilon_{\text{all}}(p/p_0) = (1 - 2\nu) \phi_{\text{mic}} E_{\text{wall}}^{-1} \sigma_{\text{mic}}(p/p_0) + \frac{1}{E_{\text{mic}}^{-1} - \phi_{\text{meso}}}
\]

\[
\varepsilon_{\text{all}}(p/p_0) = (1 - 2\nu) \phi_{\text{mic}} E_{\text{wall}}^{-1} \sigma_{\text{mic}}(p/p_0) + \frac{1}{E_{\text{mic}}^{-1} - \phi_{\text{meso}}}
\]

\[
[(1 - x)\sigma_{\text{mic}}(p/p_0) + 2(x - \nu)\sigma_{\text{mic}}(p/p_0)]
\]

(13)

In addition to the parameters already obtained from the modeling of the adsorption isotherm (\(d\) and \(b\)), the parameters \(\partial b/\partial E_{\text{mic}}\) (appears in \(\sigma_{\text{mic}}\) eq 9) and \(E_{\text{mic}}\) are adapted, whereas \(x = 0.32\) and \(\nu = 0.2\) are considered as given. We stress that \(E_{\text{mic}}\) is just an overall scaling factor for the strain isotherm and, as such, its value has no impact on the shape of the strain isotherm. On contrary, the parameter \(\partial b/\partial E_{\text{mic}}\) determines the ratio of the strain minimum to the strain maximum at saturation pressure. This allows for a straightforward fitting process: first, we normalize the strain isotherms to their respective values at the saturation pressure, and then we adjust the values for \(\partial b/\partial E_{\text{mic}}\) and \(E_{\text{mic}}\) to reproduce the initial contraction and to match the experimental net strain at saturation pressure. The modeling of the strain isotherm of the sample Calc according to eq 13 is shown in Figure 3 on linear pressure scale and Figure 4 on logarithmic pressure scale; the respective results for the samples Sint750 and Sint850 are given in Figures S1, S2, S4, and S5. All parameters are given in Table 2, and \(E_{\text{mic}}\) is also included in Figure 5.

As can be seen from Figures 3 and 4, the simple micropore model gives only an approximate description of the adsorption isotherm, whereas the mesopore adsorption/deformation is well modeled. A major issue is that micropore size distribution of the materials investigated is probably rather broad, but our model employs only a single energetic parameter \(b\). Consequently, micropore filling as predicted by the model occurs rather step-like, whereas the experimental data show continuous adsorption in the low relative pressure regime. This issue results in a strain minimum on the theoretical strain isotherm at higher relative pressure than seen in the experiment; however, the depth of the minimum is correctly reproduced. Notably, the strain induced by micropore filling continues over the whole relative pressure range, even for the relative pressure range above 0.1, where micropore filling in terms of additional amount adsorbed is usually insignificant.

With respect to mechanical properties, both the monolithic moduli \(E_{\text{monolith}}\) and the wall moduli \(E_{\text{wall}}\) of all microporous samples are between the extreme values of the non-microporous samples Untreated and Sint950 discussed in the previous section. Furthermore, the qualitative trend for \(E_{\text{monolith}}\) and \(E_{\text{wall}}\) is the same as for the non-microporous samples, that is, calcination and subsequent sintering both increases the Young’s moduli. Quantitatively, however, we see that the increase of \(E_{\text{monolith}}\) is larger than the increase of \(E_{\text{wall}}\); this result is different from the non-microporous samples considered in the previous section and may indicate systematic shortcomings of our micropore model. Furthermore, \(E_{\text{wall}}\) derived from the modeling process is larger than its counterpart calculated according to eq 11. Regarding the origin of the systematic error, we may assume that the energetic parameter \(b\) obtained from the modeling of the adsorption isotherm is too small resulting in a too small value for \(\sigma_{\text{mic}}\). As a result, \(E_{\text{wall}}\) is underestimated. Also, the adsorption isotherms of the microporous samples would be significantly better described by a distribution of \(b\) values (corresponding to an energetic/structural heterogeneous micropore distribution). However, this would also cause an arbitrary distribution of \(\partial b/\partial E_{\text{mic}}\). An obvious solution for this issue would be the application of a more sophisticated micropore model in future work.

Finally, we shortly comment on the stiffening of the mesopore walls as a consequence of sintering. Whatever scaling law for the modulus—wall microporosity relation (see e.g., ref 57) would be applied, the change in wall microporosity would not be sufficient to explain the drastic changes in the wall Young’s modulus. Therefore, the observed stiffening must take place at the level of the silica network itself. Scherer17 has reported a similar unexpected increase of the Young’s modulus in Vycor porous glass upon sintering at 800 °C. As we do not have an alternative explanation, we follow here the argument of Scherer by attributing the modulus increase to the condensation of hydroxyl groups, leading to the elimination of nonbridging oxygen and consequently to a stiffening of the mesopore walls.

4. CONCLUSIONS

We have successfully implemented a micropore model into the theoretical framework of adsorption-induced strains in meso- and macroporous solids proposed earlier37 to describe the deformation of silica monoliths with hierarchical porosity at different scales. This enabled the successful evaluation of the elastic moduli for micro—meso—macroporous samples from in situ dilatometry during \(N_2\) sorption and their comparison with macroscopically derived mechanical parameters. We found a systematic increase of the Young’s moduli of both the pore walls, \(E_{\text{wall}}\), and the monolithic samples, \(E_{\text{monolith}}\) upon calcination and sintering. Our results suggest that the stiffening of the mesopore walls is the primary reason for the stiffening of the monoliths.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b03242.

\[N_2\] adsorption isotherm at 77 K and corresponding strain isotherm for additional silica samples (PDF)

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