Abstract: We present a modeling scheme to analyze cagelike silica mesoporous crystals based on in situ X-ray diffraction (XRD) data collected during gas adsorption–desorption (physiosorption) processes. Nitrogen physisorption on a silica mesoporous crystal of SBA-16 was directly monitored by using synchrotron in situ powder XRD measurements conducted at SPring-8. SBA-16 is a well-ordered mesoporous silica in which three-dimensional interconnected cagelike primary mesopores are located at the body-centered cubic lattice points. In addition, the surrounding silica matrix contains random microporous and mesoporous intrawall porosities that are significantly influential to the diffusion properties, and thus important to be quantified for this media. The in situ XRD data exhibits seven Bragg reflections throughout the measurements, and the present method allows one to obtain the maximal and stand-alone information about the pore structure (for example, the mesopore size, the matrix density, the intrawall porosity, and pore surface roughness) together with the nitrogen film evolution in the primary mesopores and the intrawall pore-filling in the silica matrix. We furthermore observe a macroscopic amount of nitrogen adsorbed assuming the density of the fluid, and confirm that the XRD “isotherm” recalculated from the analysis result is consistent with the conventional nitrogen isotherm on a semi-quantitative level; however, these results suggest that the intrawall pores would have a greater contribution to the adsorption than considered based on the conventional isotherm analyses. The present method is readily extendable to any ordered mesopores wrapped by the wall matrix containing a certain intrawall porosity.

Keywords: intrawall porosity · mesoporous materials · physisorption · SBA-16 · X-ray diffraction

Introduction

Ordered mesoporous silicas,[1] or silica mesoporous crystals, have attracted much attention as promising materials for a broad range of technological and biological applications.[2] Mesoporous crystals exhibit various two- (2D) and three-dimensional (3D) crystallographic symmetries in terms of the arrangement of primary mesopores showing long-range translational order (termed regular mesopores), whereas there is no ordering at the atomic scale. When amphiphilic block copolymers are used as the structure-directing agent for the preparation of silica mesoporous crystals, it is known that a significant amount of random intrawall pores are present within the silica wall matrix, wrapping the regular mesopores.[3,4] For maximal usage of such crystals, it is important to estimate not only the regular nanopore morphology, but also the disordered intrawall pore structure, including the silica matrix density and pore surface roughness. Gas
adsorption isotherms have been extensively applied to mesoporous crystals, from which various aspects about the porous solids can be derived.\[5\] The adsorption isotherm measurements themselves supply robust experimental data. Most analyses are strongly dependent on assumptions, such as pore geometries and various empirical parameters fitted from standard isotherms to express the fluid state\[5\] and thus the obtained structural information is often indirect.

In this regard, electron crystallography and small-angle X-ray diffraction (XRD) approaches are particularly suitable for obtaining direct structural information of mesoporous crystals. Electron crystallography allows the direct reconstruction of the 3D structure based on transmission electron microscopy (TEM) images for which assumptions about the pore shape and connectivity are not required.\[6,7\] XRD is a powerful tool for investigating the mesopore structures on a quantitative level, for which modeling methods are commonly adopted to evaluate the pore wall structure, because of the limited diffraction information (from several Bragg reflections) arising from the structural fluctuation that is an inherent nature of mesoporous crystals.\[3,4\] Moreover, XRD studies coupled with gas adsorption measurements (in situ XRD)\[9\] have recently attracted significant attention as a yet another technique to investigate the physisorption process of mesoporous crystals. Much effort has been devoted to the analyses of these in situ XRD data to extract the structural information about the pore wall, as well as the adsorbate forming the fluid film in nanopores.\[10-16\] These data have been analyzed by modeling the regular mesopore on a lattice, wall porosity, and/or the pore wall roughness, which were fitted to the intensities obtained from the limited number of observed diffraction peaks. Besides the diffraction data, Jahner et al. demonstrated a sophisticated usage of the baseline arising from the diffuse scattering, enabling the evaluation of the disordered intrawall porosity in the silica matrix.\[16\] In these attempts, the adsorption isotherm data were often adopted as the complement to in situ XRD analysis, which provided a better insight, compared to ordinary XRD, into the pore wall structure and adsorption process in the mesoporous crystals. However, there have been no in situ XRD analyses that quantitate self-consistently the pore wall structure and the fluid film structure upon the adsorption. It would be interesting if such structural information could be obtained in a self-consistent manner within an analysis regime for in situ XRD experiments.

In this study, we present a stand-alone scheme devoted to the maximal usage of in situ XRD data collected during the nitrogen adsorption on cage-like silica mesoporous crystal SBA-16. SBA-16, a member of the SBA-\(n\) family,\[17-19\] is a 3D silica mesoporous crystal that consists of a network of large cage-like mesopores placed at the body-centered cubic lattice points within the space group Im\(\overline{3}\)m.\[20\] Due to the use of block copolymers during the synthesis, SBA-16 possesses intrawall pores that surround the regular mesocages.\[21\] This intrawall porosity is analogous to that known for 2D cylindrical mesoporous crystal SBA-15 with the plane group \(p6mm\).\[3\] The Brunauer–Emmet–Teller (BET) surface area of SBA-16 is normally in the range of 400–900 m\(^2\)g\(^{-1}\).\[18,21–23\] Kleiz et al. reported that the measured BET surface area of SBA-16 notably originates from the intrawall porosity within the silica wall matrix.\[21\] and thus this intrawall porosity has considerable influence on the diffusion properties as well as the ordered mesopore morphology.\[24\] Gobin et al. reported that the diffusivity of SBA-16 is unexpectedly higher than that of SBA-15 despite the limited size of entrances between the mesopores.\[25\] It is indeed highly important to assess the precise pore structure that can be parameterized by the mesopore arrangement, mesopore size, connectivity, latent intrawall porosity, density of wall framework, and so forth.

In the main part of this paper, we develop a simplified model for an uptake of adsorbate on a cubic network of spherical regular mesopores surrounded by the intrawall porosity. We further incorporate the effect of the structure fluctuation as a result of the mesopore surface roughness, the lattice, and the pore-shape fluctuations. It will be shown that, within the limited diffraction information from SBA-16, the full aspects of the pore wall structure can be quantitatively analyzed through analyzing the whole set of in situ powder XRD data simultaneously. Also, the analysis allows one to monitor the nitrogen adsorption process in both the intrawall and regular mesopores. Assuming a constant density of the confined fluid, we quantify the macroscopic amount of nitrogen adsorbed at respective pressure steps. The density contrast obtained from respective pressure steps gives an account for the silica wall matrix density, intrawall porosity, and the true density of silica, whereas the insight to the regular mesopore lattice and the fluid evolution on it is derived in a similar way to the standard modeling schemes as introduced by the above references. Accumulation of these results represents the self-consistent picture of nitrogen filling in the pore wall structure of SBA-16. While previous in situ XRD studies focused on 2D hexagonal structures, such as MCM-41 or SBA-15 materials,\[12,14-16\] for the first time to our best knowledge we apply in situ XRD analysis to a 3D cage-type mesoporous crystal.

Results and Discussion

Preliminary characterization: The nitrogen isotherm measured on the calcined SBA-16 is shown in Figure 1a. The isotherm demonstrates a clear H2-type hysteresis loop,\[20\] composed of a gradually ascending adsorption branch, and a steeply descending desorption branch. This trend is typical for ink-bottle pores.\[21,26,27\] This stepwise desorption is associated with the cavitation of metastable condensed nitrogen at the relative pressure \(P/P_0\approx0.47\), which induces spontaneous evaporation.\[28\] The cavitation mechanism suggests that the size of entrance to the primary mesopores must be smaller than 4 nm.\[29,30\] A noticeable increase of the volume adsorbed \((V_{ads}\text{ cm}^3\text{(STP)}\text{ g}^{-1})\) beyond the hysteresis loop continues up to the saturation at \(P/P_0=1\), suggesting that this SBA-16 possesses a considerable quantity of large
meso- or macropores. The presence of such pores is confirmed by scanning electron microscopy (SEM) observation as described later. The BET surface area [31] (calculated from $P/P_0 = 0.05–0.30$) and the total pore volume (measured at the single point $P/P_0 = 0.99$) are 578 m$^2$ g$^{-1}$ and 0.532 cm$^3$ g$^{-1}$, respectively. The pore size distribution (PSD) was calculated by using nonlocal density functional theory (NLDFT) of a spherical pore geometry [30] based on the adsorption branch, and the result is shown in Figure 1b together with the cumulative pore volume. The employed NLDFT scheme assumes a spherical pore geometry for a pore diameter $> 5$ nm, and a cylindrical pore geometry otherwise. [30] A broad peak around 2–5 nm and a relatively sharp peak around 9.4 nm are observed, implying the presence of uniform mesocages and non-uniform intrawall pores. The mean diameter of spheroidal mesopores is determined to be 9.416 nm with 0.3% of the fitting error of NLDFT to the experimental isotherm. The Barrett–Joyner–Halenda (BJH) method, which has been mostly employed in PSD analysis among mesoporous solids, was also conducted only for comparison with NLDFT values. It is known that the BJH method may underestimate the mesopore diameter, by up to 100% in the case of spherical pore geometry, [30] and the BJH value from the adsorption branch indeed gave the pore diameter of 5.6 nm.

A comparative $\alpha_s$-plot analyzed from the isotherm is given in Figure 1c along with the plot of their slopes. Conversion from the isotherm to the $\alpha_s$-plot was carried out using the reference adsorbent data reported by Jaroniec et al. [32] The plot exhibits a non-linear curve that is ascribable to the presence of non-uniform intrawall pores, followed by the sharp increase originating from the capillary condensation into the primary mesopores. The intrawall pore volume can be obtained from the intercept of an extrapolated straight line to the ordinate fitted in a certain range of abscissa. [33] However, nitrogen uptake in the intrawall porosity and the mesoporosity is not precisely distinguishable, since the $\alpha_s$-plot shows a gradual change in the slope. If we maximize the estimates for the intrawall pore volume by assigning the abscissa range around the minimum of the slope ($\alpha_s = 1.05–1.18$), the intrawall pore volume is 0.080 cm$^3$ g$^{-1}$. This value stays within the previously reported values (0.07–0.15 cm$^3$ g$^{-1}$) of the intrawall pore volume obtained using the same $\alpha_s$-plot method. [4] Analysis of the nitrogen isotherm is summarized in Table 1.

High-resolution SEM images are given in Figure 2 showing overviews of a) noncracked and b) cracked particles together with their close-up images, in which the macropores are clearly present, as well as the regular mesoporosity. It is observed that 1) the macro pores are randomly distributed on the external surface of the particle, and 2) uniformly

Table 1. Summary of the major pore wall structure parameters evaluated by the conventional nitrogen isotherm and mesostructural refinement on in situ XRD data using the present models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nitrogen isotherm</th>
<th>in situ XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>total pore volume [cm$^3$ g$^{-1}$]</td>
<td>0.532 (single point at $P/P_0 = 0.99$)</td>
<td>0.392(19)</td>
</tr>
<tr>
<td>intrawall pore volume [cm$^3$ g$^{-1}$]</td>
<td>0.080 (maximum by $\alpha_s$-plot)</td>
<td></td>
</tr>
<tr>
<td>mesopore volume [cm$^3$ g$^{-1}$]</td>
<td>0.397 (by NLDFT and $\alpha_s$-plot)</td>
<td>v$_p$ = 0.181(11)</td>
</tr>
<tr>
<td>specific surface area [m$^2$ g$^{-1}$]</td>
<td>576 (by BET), 254 (intrawall area by $\alpha_s$-plot)</td>
<td>v$_p$ = 0.211(8)</td>
</tr>
<tr>
<td>mesopore diameter [nm]</td>
<td>9.416 (by NLDFT)</td>
<td>134(5) (regular mesopores only)</td>
</tr>
</tbody>
</table>

Figure 1. a) Nitrogen adsorption–desorption isotherms measured at 77.4 K. b) A cumulative pore volume and PSD analyzed by NLDFT for adsorption model based on spherical pore geometry. c) A comparative $\alpha_s$-plot and its slope, for which the reference $\alpha_s$ data were taken from reference [32]. The intrawall porosity was estimated from the $\alpha_s$ range of 1.05–1.18 for the extrapolated straight line to the intercept so that the maximal estimate of intrawall pore volume is obtained.

sized regular mesopores are well-ordered inside the particle (this will be further confirmed by TEM observation below). We remark that performing high-resolution SEM on cage-like mesostructures requires more careful alignment setup than that on cylindrical mesostructures, such as SBA-15; for example, the impact electron energy on a specimen must be carefully optimized to minimize the interaction volume of the electron probe and silica wall in order to detect the signal from a depth of a few nanometers that allows us to discriminate the regular mesopores from the wall matrix.

In the nitrogen isotherm, the amount adsorbed \( V_{\text{ads}} \) at a specific pressure is made up of contributions from the intrawall porosity, the mesoporosity, and the macroporosity [Eq. (1) in which \( V_{\text{ip,me}} \) represents the amount adsorbed in the intrawall and mesopores, and \( V_{\text{macro}} \) is the amount adsorbed in the macropores].

\[
V_{\text{ads}} = V_{\text{ip,me}} + V_{\text{macro}}
\]

The existing macroporosity is not our current interest as we focus on the mesostructural detail of SBA-16. We employ the quenched solid density functional theory (QSDFT) to eliminate an influence of the macroporosity \( V_{\text{macro}} \) from the isotherm. The QSDFT model has been developed by Neimark et al. recently, and takes into account the effects of molecularly roughened surfaces on gas adsorption process.\(^{[34,35]}\) This model presents the silica wall as a diffused density distribution of solid atoms, and can predict the density profile of fluid forming on a given pore at a given pressure. The procedure is as follows. First, we assume a macropore with a single pore diameter as a representative of the macroporosity. We invoke a relationship \( V_{\text{macro}} = A_{\text{macro}} \cdot S_{\text{macro}} \) in which \( A_{\text{macro}} \) and \( S_{\text{macro}} \) are the amount adsorbed per unit area of the macropore and the specific surface area of the macropores, respectively. Figure 3a shows the calculated isotherms with different pore diameter using QSDFT. For each pore diameter, we calculate \( A_{\text{macro}} \) by using QSDFT over the whole pressure range \( P/P_0 = 0–1 \); this calculated \( A_{\text{macro}} \) is represented by \( A_{\text{DFT}} \). Second, we utilize the fact that \( V_{\text{ads}} \) of the isotherm at sufficiently high pressures \( (P/P_0 > 0.8) \) originates only from the macroporosity. In this case, Equation (1) can be modified as to give Equation (2).

\[
V_{\text{ads}} = \text{constant} + \frac{A_{\text{DFT}}}{S_{\text{macro}}} \]

By fitting Equation (2) to the experimental isotherm data in the range of \( P/P_0 > 0.8 \), we obtain \( S_{\text{macro}} \) for each pore diameter. The pore diameter of 500 nm gave the best fit, and was chosen as the representative for the existing macroporosity. In this case the specific surface area of the macroporosity is estimated as \( S_{\text{macro}} = 54.6 \text{ m}^2\text{g}^{-1} \). Third, \( V_{\text{macro}} = A_{\text{DFT}} \cdot S_{\text{macro}} \) calculated by QSDFT over the whole pressure range was subtracted from the experimental isotherm so that the contribution of the macropores is eliminated. This isotherm \( V_{\text{ip,me}}(p) \) is shown in Figure 3b. We call it a “modified isotherm” in the following.

Figure 2. SEM images of the SBA-16 crystal. a) Random macro pores observed on the external surface of non-cracked particles. b) Regular mesopores observed on a cracked surface showing the internal part of the particles.

Figure 3. a) Calculated isotherms for spherical macropores predicted by QSDFT at different pore sizes. b) The “modified isotherm” in which the macropore contribution is eliminated from the original isotherm. See the main text for details.
We used TEM to assess the crystallinity of the sample, and furthermore we have analyzed the obtained TEM images by electron crystallographic reconstruction, which gives a three-dimensional view of the crystal unit cell based on the relevant space group. The detailed image processing of electron crystallography for mesoporous crystals can be found elsewhere.[6,7] Figure 4a–c shows the TEM images taken along the principal crystallographic zone axes; an excellent mesoporous order is observed over a large area, endorsing that the sample crystallinity is high enough to apply the XRD toward the structural quantification. The electrostatic potential map reconstructed based on those images is depicted as the contour plots in Figure 4d and e. These plots suggest that the pore shape of this SBA-16 crystal is very spherical, which further supports that the assumption of spheroidal mesopore shape is appropriate, and underpins the validity of the mesostructural modeling carried out in the next section.

**In situ powder XRD:** Besides the conventional nitrogen volumetric isotherm measurement, the nitrogen physisorption process on SBA-16 was monitored by in situ synchrotron powder XRD. The approach is fully independent from the analysis on the isotherm. The in situ XRD patterns during the nitrogen adsorption and desorption processes are plotted in Figure 5. Seven Bragg reflections are identified throughout the physisorption based on $I m\bar{3}m$ symmetry of SBA-16, whereby the 110 and 200 reflections possess predominant intensities. Pressure dependence of $|F(hkl)|^2$ is shown in Figure 6; the values of $|F(hkl)|^2$ were obtained after corrections to the Lorentz, multiplicity and scale factors were applied. The change in $|F(hkl)|^2$ originates from the alteration of the electron density due to the uptake of nitrogen into the silica pore wall. The spatial distribution of adsorbed nitrogen presumably possesses the same $I m\bar{3}m$ symmetry as the mesopore system.

To quantify the amount of nitrogen adsorbed in SBA-16, we employ an analytical model[3,12–16] for expressing the meso and the intrawall porosities, as well as the nitrogen fluid structure as a function of the pressure. Analytical modeling for the wall architecture of ordered mesoporous silicas was introduced in 2000 by Imperor-Clerc et al.,[3] who established a scheme for describing the mesopore structure of 2D hexagonal SBA-15 materials (cylindrical mesopore surrounded by intrawall pores). The scheme was further extended for analyzing gas adsorption processes on 2D hexagonal MCM-41[12,13] (cylindrical mesopores) or SBA-15[13,14]...
(cylindrical mesopores surrounded by random intrawall porosity) by means of in situ XRD coupled with sorption experiments. Herein, we first modify the above scheme toward a 3D cubic crystal system by representing cagelike regular mesopores of SBA-16 as spheroidal cavities, and further incorporating the intrawall porosity as being uniformly distributed within the wall matrix. Moreover, a scheme is established so that the macroscopic amount of nitrogen adsorbed is obtained by utilizing the density information. It should be noted that the number of structural parameters used in analytical modeling has to be minimal due to the limited number of detectable Bragg reflections from the mesostructure.

In the modeling below, we use a term density as a mass density for convenience even though XRD reflects the electron density distribution. Note that a mass density is readily converted to the corresponding electron density by multiplying a factor equal to \( \frac{\text{atomic number}}{C_148 \times \text{Avogadro constant}} / \text{molar mass} \). The computational scheme is straightforward. First, we introduce the intrawall pore fraction \( f_p \) (0 \( \leq f_p \leq 1 \)) to represent the average density of the wall matrix. The average wall density under “dry” conditions (intrawall pores are empty) \( D_{\text{wall,dry}} \) and totally “wet” conditions (intrawall pores are totally filled with nitrogen) \( D_{\text{wall,wet}} \) are then given by Equations (3) and (4) in which \( D_{\text{fluid}} \) and \( D_{\text{SiO}_2} \) stand for the fluid density of nitrogen and the true density of amorphous silica, respectively.

\[
D_{\text{wall,dry}} = (1 - f_p) D_{\text{SiO}_2} \quad (3)
\]

\[
D_{\text{wall,wet}} = f_p D_{\text{fluid}} + (1 - f_p) D_{\text{SiO}_2} \quad (4)
\]

Equations (3) and (4) can be generalized for partially “wet” wall density as Equation (5) in which \( \eta \) represents the nitrogen filling rate within the intrawall porosity: 0 \( \leq \eta \leq 1 \).

\[
D_{\text{wall}} = \eta f_p D_{\text{fluid}} + (1 - f_p) D_{\text{SiO}_2} \quad (5)
\]

It should be mentioned that the true silica density \( D_{\text{SiO}_2} \) in Equations (3)–(5) is not presumed to be equal to the bulk silica density value of 2.2 g cm\(^{-3}\), which is often assumed in many other mesostructural modelings\(^{36} \). We intend to obtain \( D_{\text{SiO}_2} \) based on the present in situ XRD data only.

The SBA-16 mesostructure is modeled as an infinite periodic body centered cubic lattice in which a spherical mesopore is placed as the structural basis; the wall and fluid densities have uniform distributions. This scheme is depicted in Figure 7. Under “wet” conditions, the fluid film approximating the adsorbed nitrogen is modeled to pile up homogeneously retaining the spherical symmetry, with the increasing

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Figure 6. Plots of \( |F(hkkl)|^2 \) as a function of nitrogen gas pressure. \( |F(hkkl)|^2 \) was calculated from the integrated intensities extracted from the XRD patterns presented in Figure 5, for which the intensity normalization using the reflections from the internal standard and correction to the Lorentz and the multiplicity factors have been made.
pressure. Hence, the crystal structure $C(r)$ with the fluid growth on the mesopore can be expressed by Equation (6) in which $*$ stands for the convolution operation and $B_i(r)$ [Eq. (7)] and $B_2(r)$ [Eq. (8)] are the basis functions presenting the spherical mesopore and the empty core of the concentric fluid, respectively. $L(r)$ is an array of the delta function placed at lattice points of the infinite periodic body centered cubic. Finally a 3D Gaussian term $G(r)$ [Eq. (9)] is introduced to incorporate the effects of inherent crystallographic fluctuations of the mesopore wall system such as surface roughness\cite{32,33}, lattice fluctuation and crystallographic basis fluctuation in mesoscopic scale.\cite{33,34}

$$C(r) = D_{\text{wall}} - \{D_{\text{wall}} B_1(r) - D_{\text{fluid}} [B_1(r) - B_2(r)]\}^* L(r)^* G(r)$$

$$B_1(r) = \theta \left( \frac{\gamma a_{\text{wall}} - |r|}{2} \right)$$

$$B_2(r) = \theta \left( \frac{(1-\tau)\gamma a_{\text{wall}} - |r|}{2} \right)$$

$$G(r) = \left\{ 2\pi (\mu a_{\text{wall}})^2 \right\}^{-3/2} \exp \left[ -\frac{|r|^2}{2(\mu a_{\text{wall}})^2} \right]$$

In Equations (7) and (8), $\theta$ denotes the Heaviside step function and $\gamma$ and $\tau$ are parameterized to represent the mesopore diameter (relative to the unit cell dimension $a_{\text{wall}}$) and the fluid film thickness (relative to the mesopore radius). In Equation (9) $\mu$ is a so-called fluctuation parameter. We note here that $\mu$ may vary depending on the pressure due to the lattice deformation induced by the adsorption.\cite{33} However, we adopt merely a single refinable parameter $\mu$ throughout the in situ XRD analysis, because of the limited number of Bragg reflections, and thus the parameter $\mu$ concerns both static and dynamic fluctuation effects upon the physisorption. In the particular case of the “dry” conditions at 0 kPa, the crystal structure $C_{\text{dry}}(r)$ can be derived as Equation (10).

$$C_{\text{dry}}(r) = D_{\text{wall,dry}} - \{D_{\text{wall,dry}} B_1(r)\}^* L(r)^* G(r)$$

The Fourier transform of $C(r)$ gives the structure factor $F$ [Eq. (11)] of this system with respect to Bragg reflections inde-
Figure 8 shows the contour map of $wR$ with respect to $\gamma$ and $\mu$, and a clear minimum is perceived. This suggests that the regular mesopore structure of SBA-16 can be identified robustly in terms of the mesopore diameter and the fluctuation parameters. The mesopore diameter is about 9.2 nm, and these crudely optimized parameters are to be set as the initial input for the further optimization of the structure parameters during the nitrogen adsorption–desorption processes on regular mesopores of SBA-16 material.

**Adsorption in regular mesopores:** The adsorption into the intrawall pores plays a dominant role within the low-pressure range, and it leads to the increase of the density contrast between the wall and the empty mesopore. Indeed, the ascendant trend in intensities of predominant 110 and 200 reflections may not be explained by increase of $t$ (the growth of the fluid film). It could be rationalized instead by increase of the effective wall density. To perform the simultaneous model fitting through the adsorption–desorption process, we therefore considered the adsorption onto the regular mesopores within a pressure range that allows us to presume that the intrawall porosity was under totally “wet” conditions: $D_{\text{wall}}(p) = D_{\text{wall,wet}} = \text{constant}$. The XRD data from 0 to 30 kPa are accordingly excluded for this optimization, and $p = D_{\text{wall}}/D_{\text{wall,wet}}$. In Equation (11), the parameters $\gamma, \mu, \rho$ and $\{r(p)\}$ are simultaneously optimized under the imposed restraints of $0 < \gamma < 1, 0 < \mu < 0.2, 0 < \rho < 1$, and $0 < r(p) < 1$, in which $r(p)$ denotes $r$ at $p$th pressure step.

The results are reported in Tables 2 and 3. The value of $wR$ was minimized to be 7.00%. The mesopore diameter $\gamma_{\text{wall,cell}}$ was estimated to be 9.41(3) nm from the optimized value of $\gamma$, which is close to the NLDFT value of 9.4 nm calculated from the conventional physisorption isotherm. Determination of the optimized value of $\rho$ leads to a wall density under “wet” condition of $D_{\text{wall,wet}} = 1.75(6) \text{ g cm}^{-3}$. The intrawall pore fraction and the wall density under dry conditions were then successively obtained through Equations (4) and (3)–$f_p = 0.276(12)$ and $D_{\text{wall,dry}} = 1.53(7) \text{ g cm}^{-3}$—respectively. Once $D_{\text{SiO}_2, \gamma}$ and $f_p$ have been determined, the specific mesopore volume $v_{\text{mic}}$ and the specific intrawall pore volume $v_p$ can be calculated from Equations (15) and (16), respectively. Similarly, the specific surface area of the regular mesopores $s_{\text{mic}}$ is expressed as Equation (17).

$$v_{\text{mic}} = \frac{\pi}{3} \gamma^2 \left(1 - \frac{\pi}{3} \gamma^2\right)^{-1} (1 - f_p)^{-1} D_{\text{SiO}_2}$$  \hspace{1cm} (15)$$

$$v_p = f_p (1 - f_p)^{-1} D_{\text{SiO}_2}$$  \hspace{1cm} (16)$$

$$s_{\text{mic}} = 2 \pi \gamma^2 a_{\text{cell}} \left(1 - \frac{\pi}{3} \gamma^2\right)^{-1} (1 - f_p)^{-1} D_{\text{SiO}_2}$$  \hspace{1cm} (17)$$

Our SBA-16 is estimated to afford $v_{\text{mic}} = 0.211(8) \text{ cm}^3 \text{ g}^{-1}$ and $v_p = 0.181(11) \text{ cm}^3 \text{ g}^{-1}$, and thus the total pore volume $v_{\text{mic}} + v_p$ should be 0.392(19) cm$^3$ g$^{-1}$ if the influence from the macroporosity is excluded. The contribution to the surface area from the regular mesopores is calculated as $s_{\text{mic}} = 134(5)$ m$^2$ g$^{-1}$.

Pressure dependence of the fluid film thickness $\gamma/\gamma_{\text{wall,cell}}/2$, is plotted in Figure 9 based on the optimized data set $\{r(p)\}$. When the statistical thickness of a nitrogen monolayer (0.354 nm) is considered, roughly two layers are formed prior to the capillary condensation. The standard error increases as the fluid film builds up, and this aspect draws the following discussion. The uniform density scheme can properly approximate the fluid film structure prior to the capillary condensation; however, during and after the capillary condensation, the film thickness $\gamma/\gamma_{\text{wall,cell}}/2$ reflects the average adsorbate density distribution over the existing mesopores, and as a result $\gamma/\gamma_{\text{wall,cell}}/2$ does not correspond to a certain film thickness.

**Adsorption in intrawall porosity:** The adsorption into the intrawall porosity was studied on the basis of the pore struc-
ture parameters determined above (γ, μ, and f_ip), for which the XRD data from 0 to 30 kPa were used. Now, both the parameters ρ and τ in Equation (11) must have the pressure-dependency during the optimization: ρ(p) and τ(p).

The intrawall pore filling rate η(p) has a one-to-one correspondence with ρ(p) through Equation (5) and the definition ρ = D_fluid/D_{wall}(p). First, we decided on the initial input of [ρ(p)] by optimizing [η(p)] with a condition τ(p) = 0 in Equation (11), using the relationship given in Equation (18).

$$\frac{|F(p)|^2}{|F_{dry}|^2} = \frac{D_{wall}(p)^2}{D_{wall,dry}^2} = \frac{\{η(p)f_{ip}D_{fluid} + (1 - f_{ip})D_{SiO2}\}^2}{(1 - f_{ip})^2 D_{SiO2}^2}$$  \hspace{1cm} (18)

Afterwards, both ρ(p) and τ(p) were simultaneously refined by using Equation (11). The results are given in Table 4. It is clear that the intrawall pore filling (parameterized by η(p)) takes place gradually, whereas the fluid film growth in the regular mesopores (parameterized by τ(p)) remains nearly constant, at values that are approximately close to the formation of the monolayer.

### Table 4. Results of least-square model fitting on in situ powder XRD data. Growth of the fluid film and intrawall pore filling during the adsorption into the intrawall porosity.

<table>
<thead>
<tr>
<th>P [kPa]</th>
<th>ρ(p)</th>
<th>η(p)</th>
<th>τ(p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.547</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.476</td>
<td>0.7529</td>
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<td>0.8035</td>
<td>0.072</td>
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<tr>
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</tr>
<tr>
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**Comparison with volumetric isotherm:** The accumulated summary of the data obtained above draws the information about the important pore wall structure as well as the scenario of the nitrogen physisorption into both the intrawall and mesopores. To assess the validity of these in situ XRD results, we estimated the nitrogen volume adsorbed, \(V_{ads}(p)\), based merely on XRD data as a function of pressure, and compared them with the modified isotherm. The information about the specific pore volumes along with \(η(p)\) and \(τ(p)\) derives the relevant volume of adsorbed gas by \(D_{fluid}\) and the nitrogen density at the standard pressure and temperature (the standard state) \(D_{SiO2}\). The pressure-dependence of \(V_{ads,XRD}(p)\) is given by Equation (19) in which \(D_{fluid}/D_{SiO2} = 646.496 \text{ cm}^3(\text{STP})\text{ g}^{-1}\).

$$V_{ads,XRD}(p) = \{η(p)v_{ip} + v_{uc}\{1 - (1 - τ(p))^2\}\}D_{fluid}/D_{SiO2}$$  \hspace{1cm} (19)

Figure 10 shows the comparison between \(V_{ads}(p)\), recalculated from the XRD results (termed XRD isotherm), and the modified isotherm (the original nitrogen isotherm data was modified using QSDFT to eliminate the influence of the existing large meso- and macropores). The XRD isotherm shows an excellent agreement with the modified isotherm. We stress here that the XRD isotherm is totally independent of the conventional adsorption isotherm measurement; no normalization or rescaling adjustments were made between these independent isotherms. The total contribution from the intrawall porosity was evaluated to be \(v_{ip}D_{fluid}/D_{SiO2} = 117 \text{ cm}^3(\text{STP})\text{ g}^{-1}\), and the intrawall pore filling is indicated within Figure 10. This contribution amount is about 2.3 times higher than the maximum estimate by the \(\alpha_s\)-plot corresponding to the specific intrawall pore volume of 0.080 \text{ cm}^3\text{ g}^{-1}. Considering that the primary mesopore size and the nitrogen adsorption quantity evaluated by XRD conform with those evaluated by the adsorption isotherm over the whole pressure range, this in situ XRD result suggests that a greater amount of void space may exist within the wall matrix compared to the intrawall pore volume derived by the \(\alpha_s\)-plot. It should be mentioned here that the mesostructural modeling above is based on a definite boundary between the spherical regular mesopores and the uniform silica matrix along with the fluctuation parameter, whereas the \(\alpha_s\)-plot method relies on the standard \(\alpha_s\)-curve obtained from the nonporous reference material, and thus applicable to the observed isotherm without geometrical assumptions. More experiments are required in order to dis-
from the convolution of the optimized electron density profiles EDP(s) derived from the present results (Figure 11). Here the electron density profiles of solid and fluid at various pressures during nitrogen adsorption and desorption processes. The effective wall densities under “dry” (1.53 g/cm³) and “wet” (1.75 g/cm³) conditions are indicated in a). The average radius of a regular mesopore (4.705 nm) is indicated in b). Likewise, a total degree of structural fluctuation (including surface roughness, lattice and basis deviations, and the possible lattice deformation induced by the pore filling) was estimated to be 1 nm.

Figure 11. Electron density profiles of solid and fluid at various pressures during nitrogen a) adsorption and b) desorption processes. The effective density of the solid wall matrix. In Figure 11a, two cases under “dry” (the intrawall pore is empty) and “wet” (the intrawall pore is filled) conditions are indicated with the corresponding mass densities. From the solid density profile of the “wet” wall, the value of 1 nm is evaluated as a result of the mesostructural fluctuation of SBA-16, which involves not only the surface roughness but also deviations of the pore size, the lattice points, and the shape of the pores. These deviations can be static (inherent in the solid pore structure) and also dynamic (deformation induced by the uptake of nitrogen during the physisorption). Further detailed study is necessary to distinguish individual fluctuation effects, which require a more crystalline sample in order to obtain more Bragg reflections. The adsorbed film is formed within the regular mesopores simultaneously with the intrawall pore filling. At a pressure higher than 30 kPa (intrawall pores are presumed to be completely filled), the adsorption film builds up gradually prior to the capillary condensation that occurs at the gas pressure of 67–72 kPa, as seen from the electron density profiles shown in Figure 11.

Conclusion

The precise pore wall structure and the nitrogen uptake process on a 3D cagelike mesoporous crystal structure of SBA-16 was studied primarily by means of in situ powder XRD for nitrogen adsorption–desorption based on the simplified analytical model developed for the cubic network of spheroidal mesopores surrounded by the random intrawall porosity. The inherent intrawall porosity and its influence on nitrogen adsorption were emphasized, which requires further exemplification to establish a true picture of the intrawall porosity in SBA-16. By comparing the Bragg intensity data collected under “dry” conditions (i.e., all pores are empty) and completely “wet” conditions (all pores are completely filled with nitrogen), we first determined the true density of the silica involved in the porous wall matrix. Then, the nitrogen physisorption process was finely traced by analyzing the Bragg intensities with the analytical model as a function of the gas pressure, followed by the derivation of various parameters, not merely for the evolution of the nitrogen film, but also the accurate mesopore structure of SBA-16 as well as the intrawall porosity distributed within the silica wall matrix. On the basis of the information obtained above (the pore structure parameters, fluid film evolution, and true density of silica), we recalculated the macroscopic amount of nitrogen adsorbed (XRD isotherm); all the results drawn from the analyses were fully independent of the other characterization methods. The only assumption that we made was the constant density of nitrogen fluid of 0.807 g/cm³. The existing macroporosity on the external particle surfaces, which was clearly seen by SEM, should be discriminated from the intrawall and mesopores in order to discuss the primary crystal structure of SBA-16 in com-
parison with in situ XRD analysis. The QSDFT calculation was employed to eliminate the macroporosity effect on the isotherm, and the predicted isotherm was properly subtracted from the experimental one (modified isotherm). Then, we could directly compare the XRD isotherm with the modified isotherm. The result showed a good agreement on a semi-quantitative level. Finally we stress that the overall scheme of the present method is general and applicable, depending on the number of observable diffraction peaks, to other ordered mesoporous networks enclosed in cavernous solids that are essential to the intrinsic diffusion properties.

Experimental Section

Synthesis of SBA-16: SBA-16 samples were synthesized using poly(ethyl-ene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers (BASF Pluronic F127, EO106PO70EO106) as a supramolecular template similar to that originally reported by Zhao et al.[20,26] Tetraethyl orthosilicate (TEOS, 98%, Acros) was used as the silica source under acidic synthesis conditions. An aqueous solution of copolymers was prepared by first adding hydrochloric acid to distilled water and then dissolving the copolymers. TEOS was then added with magnetic stirring at 308 K. The starting molar composition was 0.0040 F127:1.0 TEOS:4.0 HCl:130 H2O. The mixture was stirred for 15 min until the TEOS was completely dissolved. The mixture was then placed in an oven for 24 h under static conditions at 308 K for precipitation of the product. The mixture was further maintained at 373 K for 1 day for hydrothermal treatment. The white solid precipitate was isolated by filtration without washing and dried at 373 K. The product was subsequently calcined under air at 823 K after washing with ethanol in order to remove the copolymer template.

Nitrogen adsorption-desorption isotherm: The nitrogen adsorption-desorption isotherm was measured at 77.4 K on a ASAP2020 Instrument (Micromeritics). Prior to the measurement, the calcined SBA-16 sample was degassed at 453 K for 10 h under vacuum. The BET specific surface area was evaluated from the adsorption data in the relative pressure range from 0.05 to 0.30. The total pore volume was estimated from the adsorption branch model). The intrawall porosity was analyzed based on the aij plot methodology.[27] The macroporosity was estimated by using QSDFT,[28,29] assuming the spherical pore geometry. A dedicated program for QSDFT was developed by Y.L.

Electron microscopy: SEM images were taken using a JSM-7401F (JEOL Ltd.). The sample of calcined SBA-16 was gently crushed to observe both external and internal surfaces. Without coating the sample, the subsequent SEM observation was carried out with a gentle-beam mode at a relatively short working distance (1.4 mm) and a low landing voltage of 0.6 kV, whereby landing voltage = accelerating voltage – stage-bias voltage.[30] TEM observation was conducted by using a JEM-3010 (JEOL Ltd.), operating at 300 kV (Cs 0.17 nm). The observed profiles (Figure 5) were analyzed by using the split-type Pearson VII function implemented in a refinement program developed by Y.K., in order to extract the scale factors and to obtain the integrated intensities of Bragg reflections. As a consequence of the pattern fitting, the cell parameter a000 of SBA-16 regular lattice was determined to be 15.3 nm. Least-square meso-structural model fitting to the F(2kO) 2 data set (Figure 6) was performed using dedicated program modules developed by K.M., in order to analyze the pore structure parameters and the nitrogen fluid evolution as well as the uptake as the intrawall porosity.

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