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# Effect of synthesis time and treatment on porosity of mesoporous silica materials

**Asli Ertan · Pradeep Kodumuri · Orhan Talu ·**
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**Abstract** Nitrogen adsorption at 77 K on mesoporous silica materials (MPS) with varying synthesis time and treatment conditions was investigated. Scanning electron microscope (SEM) and X-ray diffraction (XRD) were also used to characterize the mesoporous materials. This study was performed at 6, 24 and 72-h synthesis times. It is shown that 6-h is not enough for complete formation of the MPS material and at least 24-h is necessary. The pore structure starts decaying for the 72-h synthesis time. The three-after-synthesis treatment conditions used were 1) washed, 2) washed and calcined and 3) directly calcined after synthesis. Ethanol/HCl mixtures were used for washing and calcinations were performed at 550°C. Among these samples, directly washed sample yields the lowest adsorption capacity while washed and calcined sample yields the highest adsorption capacity. Hence, it is concluded that washing stabilizes the structure before high temperature treatment.

**Keywords** Mesoporous silica synthesis · Nitrogen adsorption · Treatment · Synthesis time

## 1 Introduction

Mesoporous silicas (MPS) have attracted considerable attention due to their numerous potential applications. MPS materials with hexagonal, cubic, or lamellar structures were invented by scientists at Mobil Corporation in 1992 (Inagaki et al. 1996; Zhao et al. 1998). These materials have ordered cages or channels and they possess high surface areas with pore diameters ranging from 1.5 to 10 nm (Kruk et al. 1997; Mou and Lin 2000). MPS materials are normally in powder form when synthesized. Recently, mesoporous silica thin films are investigated for various applications such as membrane separations, chemical sensors, optical devices etc. (Miyata et al. 2004; Lin et al. 2005). The porosity and surface area of MPS materials play a crucial role in applications using powder or thin film morphology (Miyata and Kuroda 1999). Extensive research has been performed to identify the physicochemical properties of these novel materials, the impurities they possess, as well as the consistency of their characteristics (Ekloff et al. 1999).

Physical gas adsorption of nitrogen at 77 K and at subatmospheric pressures is a commonly used and relatively simple method for characterization of surface and structural properties of porous solid materials (Wloch et al. 2002; Jaroniec et al. 1999; Kruk and Jaroniec 1997). The information obtained from nitrogen isotherms are used to determine the surface area, pore volume, pore size distribution in the micro- (0.5–2 nm), meso- (2–20 nm), and macro-pore range (>20 nm). In addition, the technique is relatively fast and robust with recently developed automated equipment. Probe gases other than $N_2$, such as Ar, $O_2$ and $CO_2$ are sometimes used as adsorptives depending on the nature of the adsorbent and the information required (Groen et al. 2003).

This study concentrates on the characterization of a series of mesoporous silicas with varying synthesis time and treatment conditions using nitrogen adsorption, scanning electron microscopy (SEM) and X-ray diffraction (XRD) to gain information about the MPS structure.

## 2 Experimental

The mesoporous silica samples were synthesized using sodium silicate, CTMABr (cetyl trimethyl ammonium bromide) and distilled water. During a typical synthesis, 150 cc distilled water was mixed with 6.57 grams of CTMABr and was stirred for 10 minutes. Then, 5.54 grams of aqueous solution of sodium silicate (14% NaOH, 27% $SiO_2$) was added drop by drop while mixing with an ultrasonic wand at room temperature for 1 hour. The mixture was placed in an autoclave and heated to 120°C for varying time intervals. After heating, the mixtures were cooled to room temperature and the pH of the mixture was adjusted to 4.83 by adding acetic acid ($CH_3COOH$).

Some of the samples were washed with HCl and ethanol solution to remove the surfactant template. Alternatively, the surfactants were removed by calcination at 550°C for 6 h with a heating rate of 50°C/15 min. Scanning electron microscopy (Amray 1820) and X-ray diffraction (Scintag X-1) were performed on part of the dried samples. Nitrogen

**Table 1** Properties of the treated mesoporous silica samples

| Treatment | Exp # | $S_{BET}$ ($m^2g^{-1}$) | $V_t$ ($cm^3g^{-1}$) | BJH avg. des. pore diameter (nm) |
|---|---|---|---|---|
| only calcined | 6 h | 678 | 0.29 | 3.1 |
| | 24 h | 739 | 0.30 | 4.2 |
| | 72 h | 43 | 0.02 | 10.8 |
| only washed | 6 h | 431 | 0.18 | 3.4 |
| | 24 h | 537 | 0.22 | 4.0 |
| | 72 h | 98 | 0.04 | 5.8 |
| washed and calcined | 6 h | 911 | 0.39 | 3.6 |
| | 24 h | 1284 | 0.52 | 4.6 |
| | 72 h | 373 | 0.16 | 5.2 |

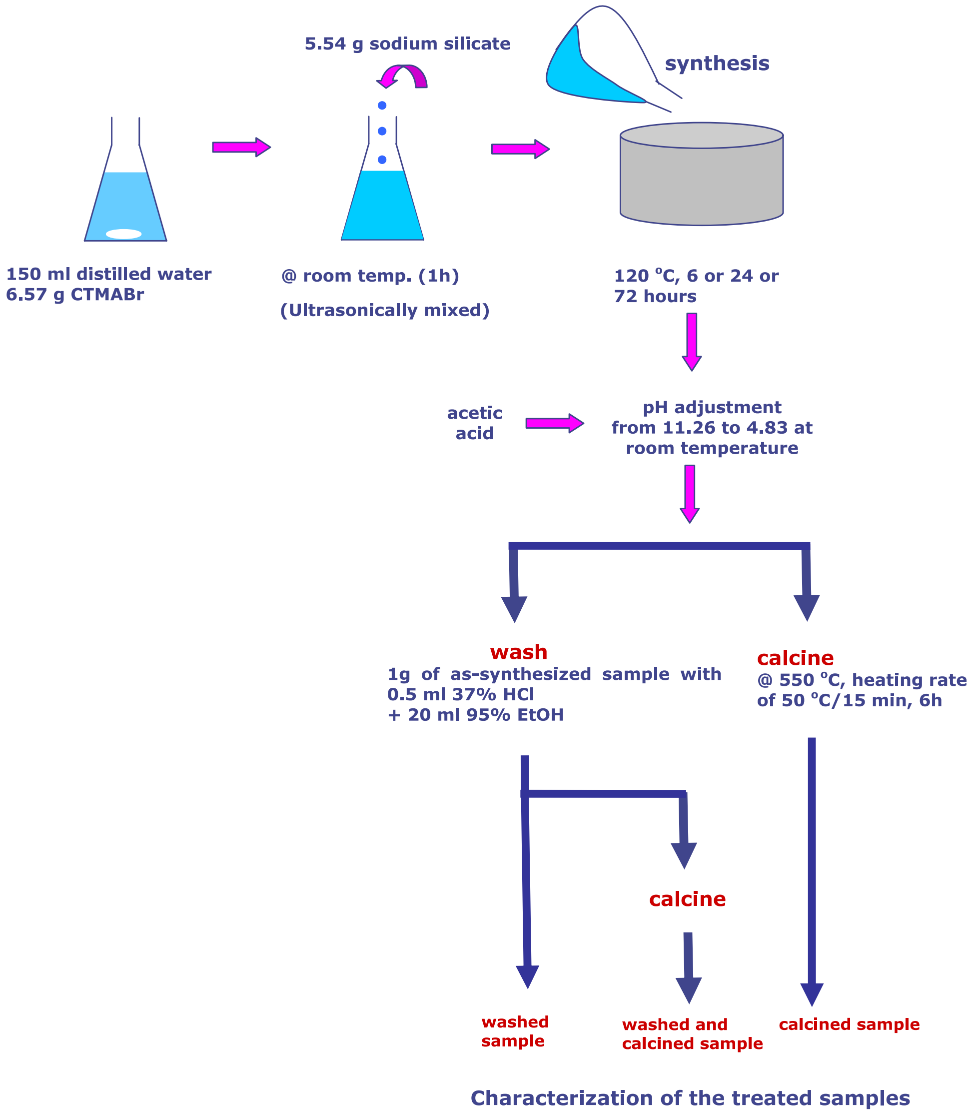


**Fig. 1** Synthesis procedure and treatment conditions of MPS materials

adsorption isotherms were measured at 77 K in the relative pressure range from $10^{-5}$ to about 1 atm with a Micromeritics 2010 volumetric adsorption analyzer. Before the adsorption analysis, the calcined samples were outgased at 250°C under vacuum of about $10^{-6}$ atm. During the activation process, complete outgassing was assured by closing the vacuum and observing the pressure for any increase.

## 3 Results and discussion

Mesoporous solids reveal adsorption isotherms showing monolayer and multilayer formation, followed by capillary condensation (types IV and V). Initially, the adsorption process is similar to that occurring on microporous solids; but, at higher relative pressures, the adsorption amount rises steeply due to the filling of the mesopores. The capillary condensation and evaporation takes place at different relative pressures which leads to the formation of a hysteresis loop on the adsorption- desorption isotherm. Normally, hysteresis due to capillary condensation is not expected to occur in well-structured homogeneous MPS materials since mesopore diameters are much smaller to support a liquid meniscus (Choma et al. 2003).

In this study, one of the parameters investigated was optimum synthesis time using 6 h, 24 h and 72 h. In addition to time, the effect of washing and/or calcination was investigated. The three treatment conditions used were; 1) washed, 2) washed and calcined and 3) directly calcined after synthesis.

Adsorption isotherms for a 6-h synthesis sample are shown in Fig. 2. As can be seen from the figure, the washed sample yields the lowest adsorption capacity while washed and calcined sample yields the highest adsorption capacity. The directly calcined sample is intermediate between the two. It is not clear why washing before high temperature calcination increases the porosity. Table 1 represents a summary of various properties of the samples under study. The same trend was observed for all samples regardless of synthesis time. One mechanism may be that ethanol/HCl washing stabilizes the structure before high temperature treatment. BET (Brunauer-Emmett-Teller) specific surface areas are 431, 678, and 911 $m^2/g$ (Table 1). Total pore volume of the samples listed in Table 1 follows the same trend. Calcined sample with 24 h synthesis time has a surface area of 739 $m^2/g$ which is consistent with the previously reported data (Araujo et al. 2005).

Sharp steps in 77 K nitrogen adsorption isotherms of MPS materials around 0.3 $P/P^o$ are commonly observed (Kruk et al. 1997). These steps are attributed to multilayer formation in well-structured homogeneous wall MPS materials. Our materials include some heterogeneity (either as mesopore size distribution and/or as surface groups) as evidenced by gradual increase in the amount adsorbed in the same region as indicated in Fig. 2. These steps become steeper with increasing synthesis time. Hysteresis loops due to capillary condensation are not observed in this study. The very small hysteresis loop above 0.95 $P/P^o$ in the isotherms is attributed to the artifact of inter-particle condensation rather than capillary condensation in the MPS particles.

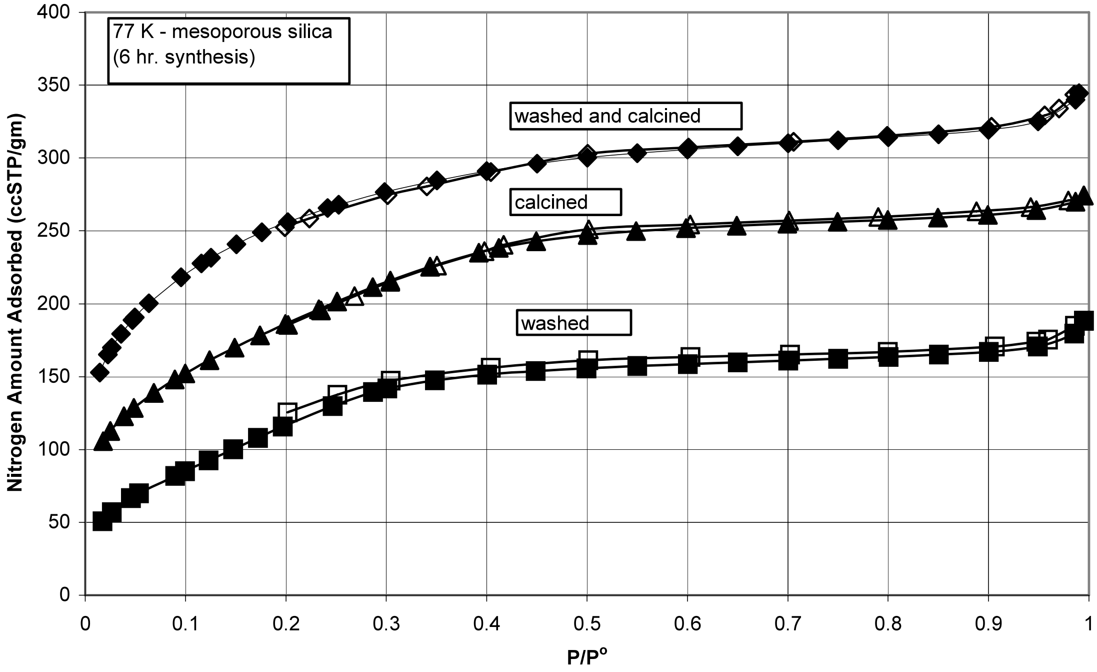


**Fig. 2** Nitrogen adsorption-desorption isotherms at 77 K for 6 h synthesis time. *Filled symbols* denote desorption

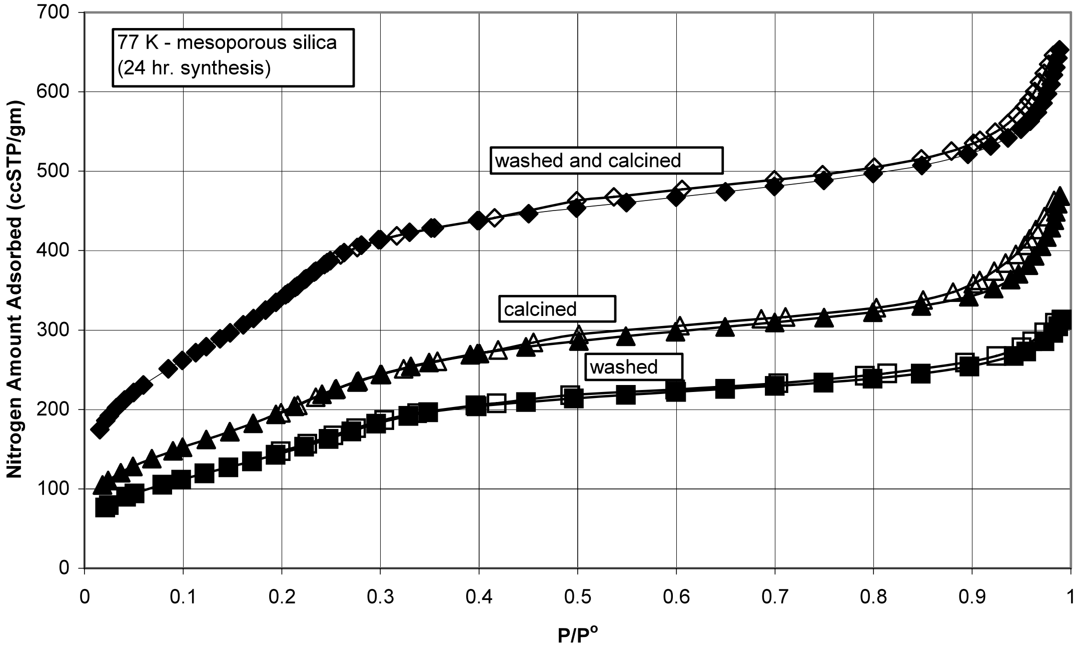


**Fig. 3** Nitrogen adsorption-desorption isotherms at 77 K for 24 h synthesis time. *Filled symbols* denote desorption

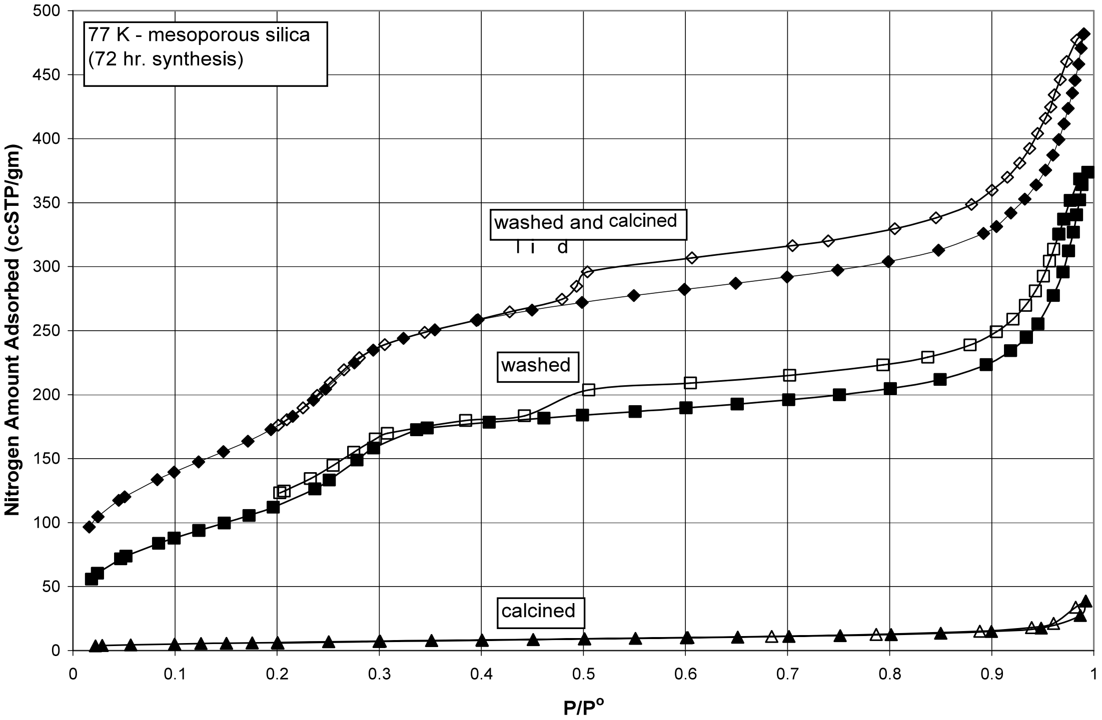
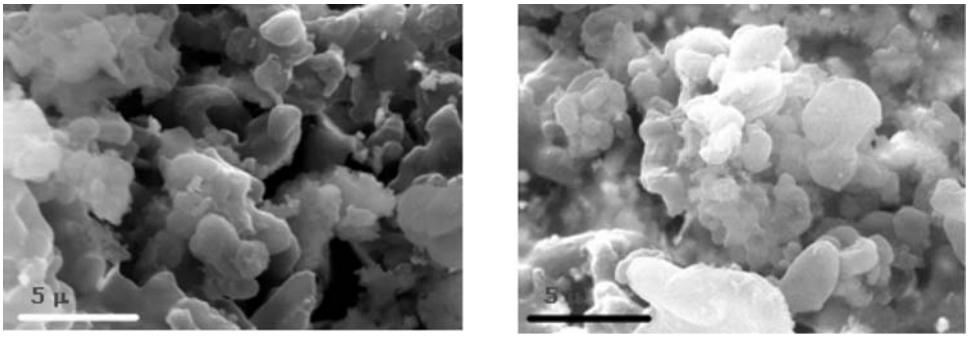


**Fig. 4** Nitrogen adsorption-desorption isotherms at 77 K for 72 h synthesis time. *Filled symbols* denote desorption

Nitrogen gas adsorption-desorption curves are presented for 24-h synthesized samples in Fig. 3. The adsorption capacities of the samples for all treatment conditions yield higher adsorption capacities in comparison to 6-h synthesis indicating that complete formation of the structure requires at least 24 hours. As with 6-h synthesized sample, washed and calcined sample yields the highest adsorption capacity and hence has the highest surface area and porosity (Table 1). The highest BET specific surface area in this study was observed for this sample with approximately

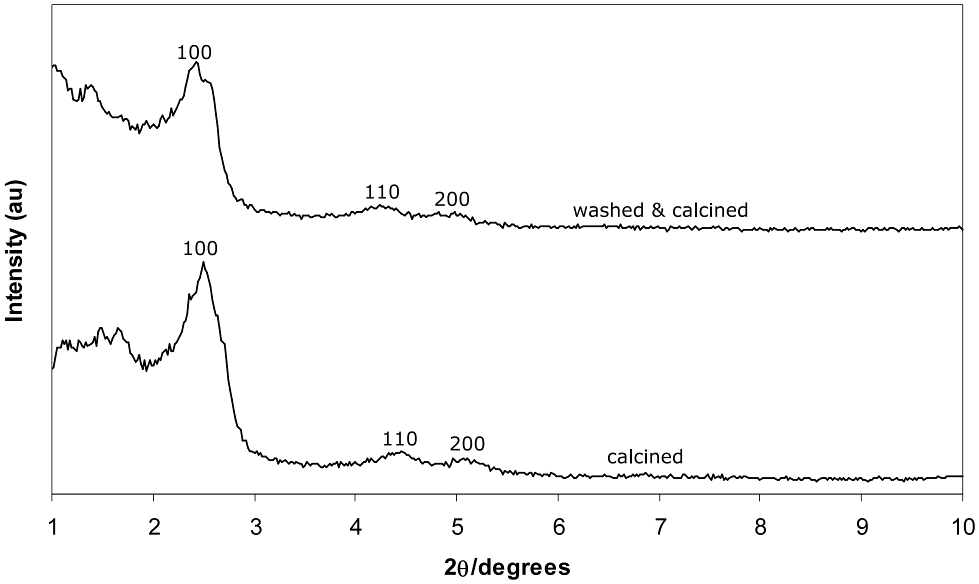
**Fig. 5** Effect of EtOH/HCl washing on crystal morphology



**a)** 24-h as synthesized

**b)** 24-h washed sample

**Fig. 6** X-ray powder diffraction pattern of the directly calcined and washed and calcined samples with 24 h synthesis time



1284 $m^2/g$. The total pore volume calculated using single point method at a relative pressure of 0.19 is 0.52 $cm^3/g$. Once again, the capacity of directly calcined sample is lower than the washed and calcined sample indicating that washing somehow stabilizes the structure. Similar specific surface area was reported for MCM-41 with 2-h synthesis time using silica gel as the silica source (Liu et al. 2008).

As the synthesis time is extended to 72 h, the structure begins to become unstable. Figure 4 shows the 77 K $N_2$ isotherms. The directly calcined sample after 72-h synthesis is completely collapsed showing very little adsorption capacity. When the samples are only washed, or washed and calcined, they have low but easily measurable adsorption capacities. Notice the enlarged hysteresis loops for these samples starting at 0.5 $P/P^{\text{o}}$ which was not observed for shorter synthesis times. This clearly indicates capillary condensation, or formation of larger pores beyond mesopore range. Some instability in the structure must be involved which results in the formation of macropores causing capillary condensation. The 72-h synthesis experiment when repeated several times yielded the same results, indicating that the instability observation is reproducible. In another study, 5 day synthesis time was found to produce higher quality MCM-41 materials as compared to the previous studies performed under analogous conditions where tetraethoxysilane was used as a silica source (Choma et al. 2002).

The SEM micrographs for all mesoporous samples indicate loose aggregate morphology consisting of irregularly shaped particles. Washing with ethanol/HCl mixture does not change the morphology although the adsorption capacities increase as discussed above (Fig. 5).

XRD analysis was performed on selected samples. Figure 6 shows an example for 24-h synthesis. Both calcined and washed and calcined samples show 100, 110 and 200 XRD peaks indicating good structural ordering. 100 peak is at a slightly higher $2\theta$ for the directly calcined sample indicating smaller pores as listed in Table 2. The small but significant shift in inter-planar spacing is another indication that washing causes structural changes which most likely stabilize the material.

**Table 2** Structural properties of MPS with 24-h synthesis time

| Treatment | $d_{100}$ (nm) | $V_t$ (cm$^3$/g) | $S_{BET}$ (m$^2$g$^{-1}$) |
|---|---|---|---|
| Calcined | 3.55 | 0.30 | 739 |
| washed & calcined | 3.60 | 0.52 | 1284 |

## 4 Conclusions

This study investigated the effect of treatment conditions as well as the synthesis time on the adsorption properties for MPS materials. It is shown that 6 h is not enough and at least 24-h synthesis time is required for the complete formation of the MPS structure. The structure becomes instable when synthesis time is extended to 72 hours. It is also shown that ethanol/HCl washing to remove the surfactant template causes slight but significant changes in interplanar spacing. This also increases the porosity of the MPS structure as well as stabilizing it to some extent.

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## Nomenclature

| | |
|---|---|
| $S_{BET}$ | BET specific surface area (m$^2$/g) |
| $V_t$ | Total pore volume (cm$^3$/g) |
| $d_{100}$ | Interplanar spacing (nm) |
| $P/P^o$ | Relative pressure |

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