Adsorption 11: 745–750, 2005

# Adsorption Monitoring of Hydrothermal and Thermal Stability of Polymer-Templated Mesoporous Materials

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**Abstract.** The thermal and hydrothermal stability of FDU-1 silica with ordered, large (∼10 nm), cage-like mesopores was studied using nitrogen and argon adsorption at −196°C. It was confirmed that FDU-1 silica retains uniform mesoporosity even after heating for 5 hours at 950–1000°C. Although typical FDU-1 silicas and other polymeric-templated silicas with large cage-like mesopores tend to be significantly microporous, the FDU-1 sample calcined at 1000°C appeared to be essentially free from microporosity, as can be inferred from the relation between its surface area, pore volume and pore diameter. This result suggests that high-temperature calcination can be used to synthesize model mesoporous adsorbents with large cage-like (spherical) mesopores. Evidence of the concomitant decrease in the pore diameter and the pore entrance size with an increase in the calcination temperature is presented. The structural stability of FDU-1 during heating in water at 100°C for 2, 4, and 8 days is additionally demonstrated.

**Keywords:** argon adsorption, ordered mesoporous silica, pore size distribution, thermal stability

## 1. Introduction

From the point of view of prospective applications of ordered mesoporous silicas (OMSs), it is important to assess their thermal and hydrothermal stability (Inagaki et al., 1993; Chen et al., 1993; Ryoo et al., 1996; Kim et al., 1998; Zhao et al., 1998; Yu et al., 2000). Many OMSs exhibit rather low hydrothermal stability and thus substantial research effort was focused on the identification of conditions suitable for the synthesis of hydrothermally stable OMSs or on the elaboration of methods to stabilize the OMS structures. The block-copolymer-templated OMSs have recently attracted much attention, which was related in part to their high hydrothermal stability attributable to their large pore wall thickness (Zhao et al., 1998; Yu et al., 2000). Gas adsorption is particularly suitable to monitor the influence of thermal or hydrothermal treatments on the porous structures of OMSs, especially as other methods, such as powder X-ray diffraction, may indicate the retention of ordered pore structure even in the case where the pore size distribution (PSD) was dramatically modified as a result of the treatment (Kruk et al., 1999; Kisler et al., 2003).

Recently, we focused our attention on the assessment and improvement of the thermal and hydrothermal stability of FDU-1 silica (Kruk et al., 2004). FDU-1 is an ordered silica with large cage-like (spherical) mesopores of diameter about 10–13 nm, which can be synthesized under acidic aqueous conditions using the poly(ethylene oxide)-poly(butylene oxide)-poly(ethylene oxide) triblock copolymer ($EO_{39}BO_{47}EO_{39}$; B50-6600, Dow Chemicals) as a template (Yu et al., 2000). FDU-1 exhibits a face-centered cubic structure (cubic close-packed; Fm3m symmetry) with 3-D hexagonal (hexagonal close-packed) intergrowth (Matos et al., 2003). It was reported on the basis of XRD (Yu et al., 2000) that

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FDU-1 retained its ordered structure even after 9 days of heating in water at 100°C, which shows its excellent hydrothermal stability. Our recent work was focused on further assessment and improvement of stability of FDU-1. To assess the thermal stability, FDU-1 samples were calcined at temperatures in the range from 540 to 1000°C and the resulting pore structures were studied using nitrogen and argon adsorption at −196°C. The hydrothermal stability of FDU-1 was evaluated on the basis of structural changes after heating in deionized water at 100°C for different periods of time ranging from 3 hours to 32 days. We have recently reported these results with some pertinent experimental data (Kruk et al., 2004). Herein, additional experimental evidence of the stability of FDU-1 is provided, the stabilization through high-temperature calcination is further discussed, experimental evidence for the pore entrance size decrease as a result of high-temperature calcination is shown, and exceptional adsorption properties of FDU-1 calcined at 1000°C are highlighted.

## 2. Materials and Methods

FDU-1 samples A and C were synthesized using $EO_{39}BO_{47}EO_{39}$ triblock copolymer as a structure-directing agent and tetraethyl orthosilicate as a silica source. The reagents were mixed at room temperature. After one day of stirring, the reaction mixture was heated for 6 hours at 100°C. The details of this synthesis procedure can be found elsewhere (Yu et al., 2000; Matos et al., 2003). In the case of sample B, a modified synthesis procedure was used. The calcination was performed under air flow with heating rate of 1°C/min and a final temperature in the range from 540 to 1000°C (provided in the notation for particular samples, e.g., A540 is the sample A calcined at 540°C), at which the sample was kept for 5 hours. The heating in water was carried out at 100°C for 2, 4 and 8 days (which is denoted as −B2d, −B4d and −B8d appended to the sample name), after which the samples were filtered out and dried at 80°C. The details can be found elsewhere (Kruk et al., 2004) Nitrogen and argon adsorption measurements were performed at −196°C on Micromeritics ASAP 2010 volumetric adsorption analyzers. Before adsorption runs, all samples were outgassed at 200°C for at least 2 hours. Adsorption data for the samples A540 and C540 have been reported earlier (Kruk et al., 2004). The BET specific surface area, pore volume and pore size distribution (PSD) were calculated as described elsewhere (Kruk et al., 1997; Kruk and Jaroniec, 2002; Matos et al., 2003).

## 3. Results and Discussion

Shown in Fig. 1 are nitrogen and argon adsorption isotherms for the FDU-1 sample A calcined at 540°C, which is a typical calcination temperature for OMSs, and at relatively very high temperatures of 950 and 1000°C. Even after these high temperature calcinations, narrow capillary condensation steps were still observed on the adsorption isotherms, and the shapes of the adsorption-desorption hysteresis loops indicated the retention of the cage-like character of the mesopores. Moreover, PSDs were relatively narrow (see Fig. 2(a)). However, the obtained materials had relatively low total pore volumes (for the samples calcined at 950 and 1000°C, 40% and 15%, respectively, of the pore volume for the sample calcined at 540°C). These

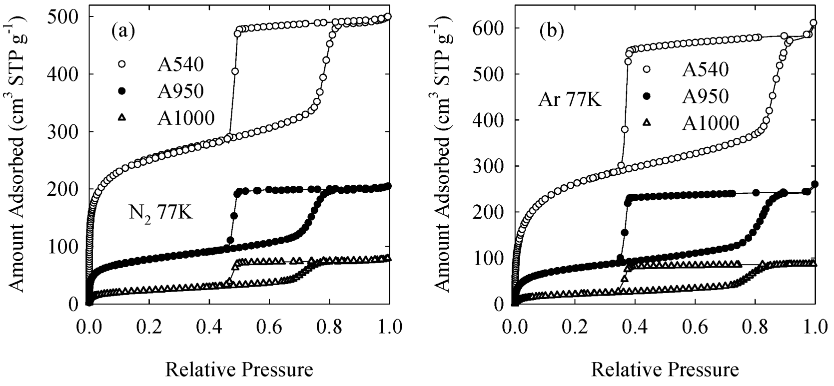

*Figure 1.* Nitrogen and argon adsorption isotherms at −196°C for FDU-1 silica sample A calcined at 540, 950 and 1000°C.

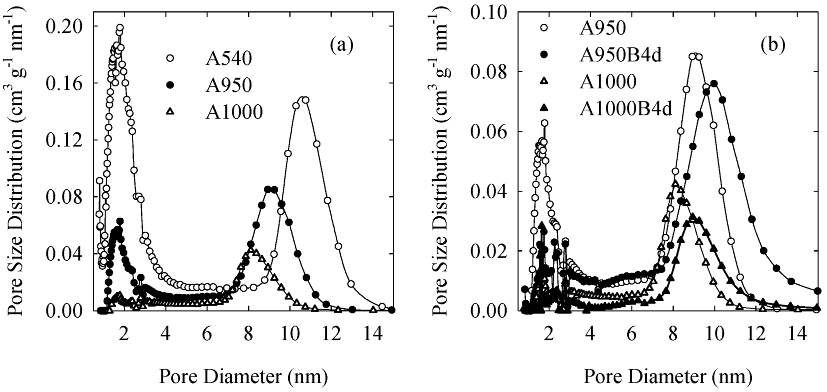

*Figure 2.* Pore size distributions calculated from nitrogen adsorption isotherm data at −196°C for FDU-1 silica sample A: (a) calcined at 540, 950 and 1000°C, and (b) calcined at 950 and 1000°C, before and after heating in water at 100°C for 4 days.

results provide confirmation of our recent report (Kruk et al., 2004) that FDU-1 samples synthesized in a way employed herein are stable for several hours under air at temperatures up to 900–950°C or even 1000°C, although they suffer an appreciable loss of adsorption capacity. The sample obtained after calcination at 1000°C exhibited very interesting adsorption properties (see Fig. 3). Namely, the increase in the adsorbed amount during the capillary condensation (the height of the capillary condensation step) was comparable to the amount adsorbed below the onset of the capillary condensation step. This is different from the behavior of a typical FDU-1 sample, for which the former amount is appreciably lower than the latter (see Fig. 1). This qualitative change in the shape of the adsorption isotherm suggests a significantly lower micropore volume for the sample calcined at 1000°C. To verify this contention, the relation between the pore diameter, pore volume, and specific surface area was examined. For ideal spherical pores, (pore diameter × surface area/pore volume) = $wS/V = 6$. In the case of a typical FDU-1 sample, [mesopore diameter×(BET specific surface area—external surface area)/(mesopore volume + micropore volume)] = $wS/V = \sim 12$. This high value is attributable to the presence of an appreciable microporosity, as micropores exhibit high (BET specific surface areas/pore volume) ratios, and therefore their presence significantly increases the numerator and has much smaller effect on the denominator in the $wS/V$ expression for the mesoporous-microporous system. The $wS/V$ value decreased to 8.2 after calcination at 950°C and to as low as 5.7 after calcination at 1000°C, approaching the theoretical value for spherical mesopores. These results suggest that the high temperature calcination may allow one to deplete or even eliminate micropores, which are formed in silicas with large cage-like mesopores templated by block copolymers due to the occlusion of the poly(ethylene oxide) blocks of the template in the silica walls during the formation of silica/copolymer composites (Ryoo et al., 2000).

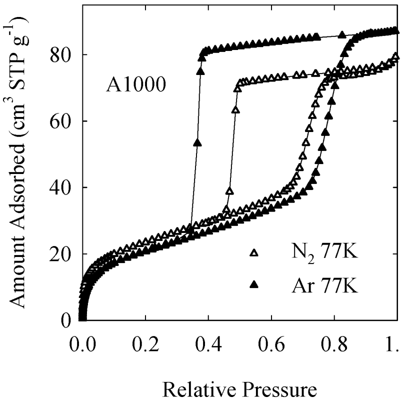

*Figure 3.* Nitrogen and argon adsorption isotherms at −196°C for FDU-1 silica sample A calcined at 1000°C.

It is well known that the pore diameter of OMSs tends to decrease as the calcination temperature increases (Ryoo et al., 2000). It is easy to verify that this decrease actually takes place for silicas with cage-like mesopores (Fig. 2(a)) (Kruk et al., 2004). However, in the case of these materials, one needs to consider another important structural property, which is the pore entrance diameter. To verify whether the entrance size also decreases as the calcination temperature increases, an FDU-1 sample was selected that exhibited capillary evaporation above the lower pressure limit of

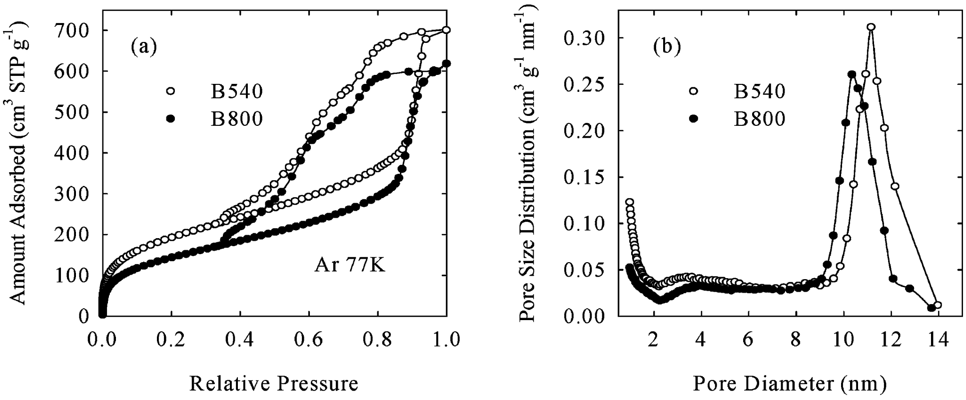

*Figure 4*. Argon adsorption isotherms at −196°C and pore size distributions calculated from them for FDU-1 silica sample B calcined at 540 and 800°C.

adsorption-desorption hysteresis. Above this limit, the desorption from cage-like mesopores takes place at a pressure of capillary evaporation from the entrances to the cage-like pores, which in turn is governed by the diameter of the entrances (Ravikovitch et al., 2002; Kruk and Jaroniec, 2003). As can be seen in Fig. 4, positions of the capillary evaporation steps shifted to lower pressures after the calcination at 800°C (in comparison to the positions of these steps for the sample calcined at 540°C). This shows that the pore entrance diameter decreases with the increase in the calcination temperature, thus following the changes in the pore diameter with temperature (the position of peak on PSD shifted from ∼11 to ∼10 nm, see Fig. 4(b)). This important result was mentioned in our earlier publication (Kruk et al., 2004), but the actual experimental evidence is presented herein.

It was reported that FDU-1 does not collapse even after 9 days of boiling in water (Yu et al., 2000). Our study further demonstrated on the basis of nitrogen and argon adsorption that uniform porosity of FDU-1 is retained even after 32 days of heating in water at 100°C (Kruk et al., 2004). The data presented in Fig. 5 illustrate this exceptional feature of FDU-1. The pore diameter increased as a result of heating in water for 2–8 days, but narrow pore size distribution persisted. The position of the desorption branch of the hysteresis loop gradually shifted to higher relative pressures, which reveals the pore entrance enlargement during the heating in water. These findings are consistent with our results for

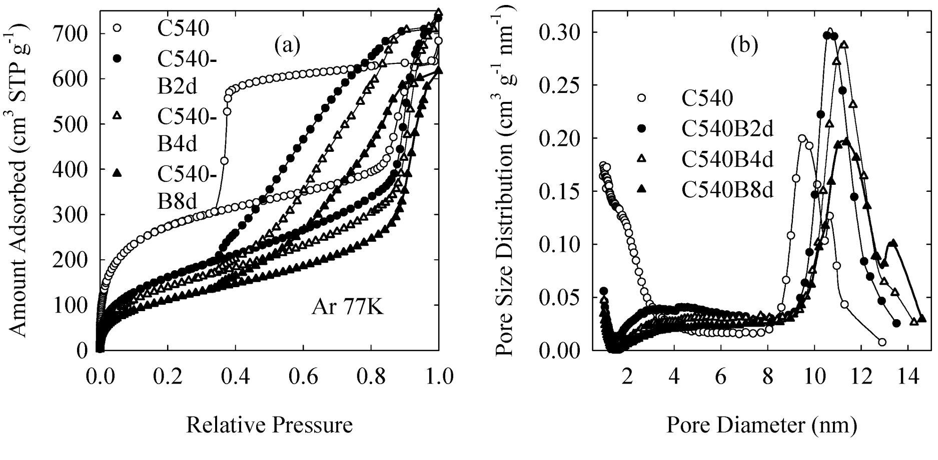

*Figure 5*. Argon adsorption isotherms measured at −196°C and pore size distributions calculated from them for FDU-1 silica sample C calcined at 540°C before and after heating in water for 2, 4 and 8 days.

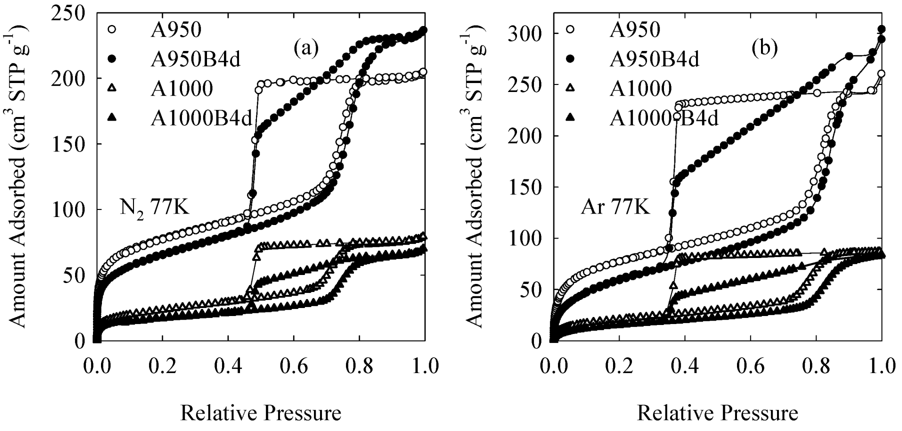

*Figure 6*. Nitrogen and argon adsorption isotherms at −196°C for FDU-1 silica sample A calcined at 950 and 1000°C, before and after heating in water at 100°C for 4 days.

another sample heated in water for periods of time from 3 hours to 32 days (Kruk et al., 2004). The pore diameter increase and the changes in the pore connectivity after the hydrothermal treatment were relatively smaller for FDU-1 samples that were calcined at 950–1000°C instead of 540°C (compare Figs. 6 and 2(b) with Fig. 5). These results additionally confirm our findings on the stabilization effects of high temperature calcination of FDU-1, which were reported earlier (Kruk et al., 2004).

## 4. Conclusions

Gas adsorption is a crucial tool for the characterization of hydrothermal and thermal stability of ordered silicas with cage-like mesopores, which allows one to study changes in the adsorption capacity, pore diameter and pore connectivity. In the case of FDU-1, nitrogen and argon adsorption data clearly indicate a facile thermal stability (up to 950–1000°C for 5 hours) and an exceptionally high hydrothermal stability. The latter appears to be further improved, when the FDU-1 sample is subjected to calcination at temperatures much higher than the typically used 540°C. The pore size and pore entrance size decrease as the calcination temperature is increased. The heating in water at 100°C has an opposite effect, leading to the pore size and pore entrance size enlargement. The heating of FDU-1 to about 1000°C appears to largely eliminate the microporosity and thus it is promising from the point of view of the synthesis of model adsorbents with large cage-like mesopores, which would not be accompanied by any appreciable microporosity.

## Acknowledgments

M.J. acknowledges support by NSF Grant CHE-0093707.

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