Adsorption (2007) 13: 323–329
DOI 10.1007/s10450-007-9072-y

Polymer-templated organosilicas with hexagonally ordered mesopores: the effect of organosilane addition at different synthesis stages

Rafal M. Grudzien · Bogna E. Grabicka · Ryan Felix · Mietek Jaroniec

Received: 2 May 2007 / Revised: 3 October 2007 / Accepted: 10 October 2007 / Published online: 31 October 2007

Abstract Two series of ordered mesoporous organosilica (OMO) SBA-15 materials with surface and bridging groups were fabricated by varying the organic precursor addition at different synthesis stages. The consequence of the delayed introduction of organic precursor on the structural and adsorption properties of the resulting OMOs was investigated. The OMOs studied were synthesized via co-condensation of tetraethyl orthosilicate (TEOS) and ureidopropyltrimethoxysilane (UPS) as well as TEOS and bis(triethoxysilylpropyl) disulfide (BTDS) in the presence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$). The aforementioned OMOs were characterized by nitrogen adsorption-desorption isotherms at −196 °C and powder X-ray diffraction (XRD). Nitrogen adsorption isotherms were used to estimate the pore volume, mesopore diameter and the BET specific surface area, whereas the XRD data provided information about structural ordering and unit cell of the samples studied.

Keywords Channel-like mesostructures · Ordered mesoporous organosilicas · Nitrogen adsorption · SBA-15 · Ureidopropyl surface group · Bis(propyl)disulfide bridging group

Ryan Felix, undergraduate student from Oberlin College (Oberlin, OH, USA) participating in the NSF-REU program during Summer 2006.

R.M. Grudzien · B.E. Grabicka · R. Felix · M. Jaroniec (✉)
Chemistry Department, Kent State University, Kent, OH, USA
e-mail: jaroniec@kent.edu

Abbreviations

a	unit cell parameter (nm)
$P_{N/S}$	nitrogen or sulfur weight percentages obtained from elemental analysis (%)
S_{BET}	BET specific surface area (m^2/g)
V_c	volume of micropores and interconnecting pores of the diameter below 4 nm (cc/g)
V_p	volume of primary pores (cc/g)
V_t	single-point pore volume (cc/g)
w_{KJS}	mesopore diameter calculated by the KJS method (nm)

1 Introduction

The incorporation of organics into ordered mesoporous silicas (OMSs) (Kresge et al. 1992; Beck et al. 1992; Grudzien and Jaroniec 2005; Grudzien et al. 2006a, 2006b) has recently become the focus of considerable attention because it introduces additional properties to those originated from a change in the surface polarity. Ordered mesoporous organosilicas (OMOs), which are of great importance for nanoscience and nanotechnology, create tremendous opportunities for catalysis (see reviews and references therein; Taguchi and Schuth 2005; Hoffmann et al. 2006; Hatton et al. 2005), adsorption, and sensing (Sayari and Hamoudi 2001; Olkhovyk and Jaroniec 2005a).

There are two major routes for the introduction of organic functionalities into OMSs. The first approach known as post-synthesis modification involves the surface functionalization of the surfactant-free OMSs (Beck et al. 1992; Feng et al. 1997; Jaroniec et al. 1998; Lim and Stein 1999), i.e., OMSs, in which the template was removed by calcination or extraction, and the surfactant-containing OMSs (An-

tochshuk and Jaroniec 1999, 2000). An important advantage of the post-synthesis modification is the possibility of tailoring of the pore diameter in OMOs by varying the size of the attached ligand (Beck et al. 1992; Feng et al. 1997; Jaroniec et al. 1998; Lim and Stein 1999).

The second approach involves co-condensation (one-pot synthesis) of appropriate organosilanes often along with either tetraethyl orthosilicate (TEOS) (Kruk et al. 2002; Gong et al. 2001; Hamoudi and Kaliaguine 2003; Lim et al. 1997) or sodium metasilicate. The latter approach became the most popular route, which yields OMSs with high concentration of functional ligands without substantial sacrificing not only mesoscopic ordering but also structural shrinkage caused by controlled calcination, which may lead to a significant decrease in the mesopore diameter, even up to 25%. The co-condensation is applied to decorate not only the surface of the pore walls but also the framework (Jaroniec 2006; Olkhovyk and Jaroniec 2005b; Grudzien et al., 2006c, 2006e); the latter materials are known as periodic mesoporous organosilicas (PMOs) (Inagaki et al. 1999; Melde et al. 1999; Asefa et al. 1999).

The main difference between the co-condensation synthesis and the post-modification of the surfactant-containing OMSs is that in the first case all precursors participate in the structure formation, while in the second case the silica-surfactant mesostructure is formed before introduction of the reactive organosilane in order to displace the surfactant template and to introduce the surface ligand. Therefore, it would be interesting to monitor the adsorption properties of OMOs prepared by adding the reactive organosilane at different stages of the mesostructure formation using the second approach, i.e., co-condensation synthesis route. It is noteworthy that a purely siliceous mesostructure of SBA-15 (silica having hexagonal arrangement of cylindrical mesopores; *p6m* symmetry group) (Zhao et al. 1998; Abu-Lebdeh et al. 1998) is formed within one hour after TEOS addition (Fulvio et al. 2005). Recently, SBA-15 with aminopropyl surface groups was synthesized using different periods (between 0 and 6 hours) for the TEOS prehydrolysis (Wang et al. 2005); the best samples were obtained by delaying the addition of organosilane from 1 to 3 hours after TEOS addition.

The current work takes advantage of adsorption technique to study the effect of a delayed addition of reactive organosilane into the synthesis gel on the adsorption properties of the resulting OMOs. This study involves the synthesis of two series of the silica-based samples with ureidopropyl surface groups and disulfide bridging groups, respectively. In addition, powder X-ray diffraction (XRD) was used to identify the structure symmetry of the resulting organosilicas.

2 Experimental

2.1 Chemicals

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) was donated from the BASF Corporation. Tetraethyl orthosilicate (TEOS) was purchased from Across Organics (98%), whereas ureidopropyltrimethoxysilane and bis(triethoxysilylpropyl)disulfide (90%; the remaining 10% contains silanes with sulfide and tetrasulfide groups) were purchased from Gelest, Inc. Deionized water (DW) was obtained using in-house Ionpure Plus 150 Service Deionization ion-exchange purification system. All chemicals were used as received without further purification.

2.2 Syntheses of mesoporous organosilicas

Ordered mesoporous organosilicas were synthesized in the presence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (P123, $EO_{20}PO_{70}EO_{20}$) by co-condensation of tetraethyl orthosilicate (TEOS) and either ureidopropyltrimethoxysilane or bis(triethoxysilylpropyl)disulfide to functionalize the surface and framework, respectively. The recipe incorporated here was analogous to the synthesis of the SBA-15 silica reported elsewhere (Zhao et al. 1998). In general, triblock copolymer P123 (2 g) was mixed with 2 M HCl (61.2 ml) and distilled water (10.8 ml) under rapid stirring at 40 °C until its complete dissolution was achieved. After 4–6 hours of mixing, either 3.858 ml or 4.07 ml of TEOS was added dropwise to the P123-HCl-DW mixture under vigorous stirring, and next 0.371 ml or 0.22 ml of ureidopropyltrimethoxysilane and bis(triethoxysilylpropyl) disulfide was added after 0, 10, 15, 20, 40, 60 and 120 minutes, respectively. The slurry was further stirred for 24 hours and aged for 48 hours at 100 °C. The powder was washed with DW, filtered and dried overnight at 80 °C. The polymeric template was extracted with 2 ml of 36 wt.% HCl and 100 ml of 95% ethanol at 70 °C. Two series of the template-free mesoporous SBA-15 silicas with ureidopropyl surface groups and bridging disulfide groups were designated as Ux and DSx, where U, DS and x relate to ureidopropyl surface groups, bridging disulfide groups and time of the organosilane addition. The name SBA-15 sample refers to unmodified calcined ordered mesoporous silica SBA-15 (see Table 1).

2.3 Measurements

Nitrogen physisorption measurements were carried out on ASAP 2010 volumetric analyzer manufactured by Micromeritics, Inc. (Norcross, GA). Adsorption isotherms were obtained in the range of relative pressures from 10^{-6}

Table 1 Selected adsorption and structural parameters for the SBA-15 silicas with ureidopropyl and disulfide groups[a]

Sample	S_{BET}, $m^2\,g^{-1}$	V_c, cc g^{-1}	V_p, cc g^{-1}	V_t, cc g^{-1}	w_{KJS}, nm	a, nm
SBA-15	866	0.11	1.18	1.38	9.78	11.5
U0	520	0.06	0.69	0.81	8.29	11.5
U10	600	0.10	0.75	0.90	8.70	11.3
U15	730	0.12	0.76	0.99	8.47	11.9
U20	625	0.14	0.64	0.90	8.27	11.7
U40	510	0.07	0.66	0.76	8.24	11.3
U60	550	0.11	0.61	0.77	8.10	11.1
U120	505	0.08	0.63	0.77	8.47	10.0
DS0	1000	0.26	0.60	1.00	6.76	10.2
DS10	970	0.23	0.78	1.07	7.68	10.0
DS15	865	0.20	0.69	0.99	7.50	9.6
DS20	930	0.22	0.67	1.02	7.00	9.9
DS40	965	0.23	0.78	1.09	7.54	10.0
DS60	750	0.17	0.66	0.90	8.27	10.8
DS120	900	0.12	1.00	1.27	9.49	11.0

[a]S_{BET}, BET specific surface area; V_c, volume of complementary pores (including micropores) of the width below 4 nm present in the mesopore walls; V_p, volume of ordered mesopores; V_t, single-point pore volume; w_{KJS}, mesopore diameter calculated by the improved KJS method (Jaroniec and Solovyov 2006); a, unit cell calculated from the observed characteristic Bragg's reflection (100). The data for SBA-15, U-15 and DS-15 samples were taken for comparison from the following reference (Grudzien et al. 2006d)

to 0.995 using high purity nitrogen at −196 °C. Prior to each adsorption measurement all functionalized silicas were degassed under vacuum for at least 2 hours at 110 °C until the residual pressure dropped to 6 or less μmHg.

Powder X-ray diffraction (XRD) measurements were recorded at room temperature using a PANanalytical, Inc. X'Pert Pro (MPD) Multi Purpose Diffractometer with Cu Kα radiation, operating voltage of 40 kV, 0.01° step size and 20 s step time over a range $0.5° < 2\theta < 3.5°$, in which a series of characteristic peaks originating from ordered mesoporosity is observed.

2.4 Calculations

The specific surface area (S_{BET}, m^2/g) for the samples under study was calculated by employing the Brunauer-Emmett-Teller (BET) method (Brunauer et al. 1938) in the range of relative pressures from 0.05 to 0.2 (Sing et al. 1985). The volume of complementary pores V_c (cm^3/g) for the SBA-15 organosilicas was calculated by integration the pore size distribution (PSD) up 4 nm, whereas the volume of ordered pores V_p (cm^3/g) was obtained by integration between 4 and the end of the PSD peak. The single-point total pore volume (V_t, cm^3/g) (Sing et al. 1985) was estimated from the amount adsorbed at a relative pressure p/p_o of 0.99, where p and p_o denote the equilibrium pressure and saturation vapor pressure, respectively. The pore size distribution was calculated from the adsorption branch of nitrogen adsorption isotherms by using the improved KJS (Kruk, Jaroniec and Sayari) method (Jaroniec and Solovyov 2006). This approach employs the BJH algorithm (Barrett, Joyner and Halenda) (Barrett et al. 1951), in which the statistical film thickness and the relation between the pore size and capillary condensation pressure (derived on the basis of adsorption data for high-quality MCM-41 materials with cylindrical pores) are used (Kruk et al. 1997). The primary mesopore diameter (w_{KJS}, nm) was defined at the maximum of PSD. The unit-cell parameter (a, nm) for the samples studied was evaluated using the XRD interplanar spacing (d, nm) values for the *p6m* symmetry group.

3 Results and discussion

3.1 Structural identification

The effect of organosilane addition at different stages of the OMO synthesis on the structural characteristics of the extracted organosilicas containing ureidopropyl surface groups and bridging disulfide groups was studied by the powder XRD in the range of 2θ from 0.5 to 3.5°. The XRD patterns for the extracted ureidopropyl-functionalized and disulfide-functionalized OMOs are shown in Figs. 1A and 2A, respectively, whereas the unit cell parameters calculated using (100) Bragg's reflection are listed in Table 1. As can be seen from Figs. 1A and 2A, an increasing delay (from 0 and 120 minutes) between the TEOS addition and the addition of reactive organosilane did not lead to any

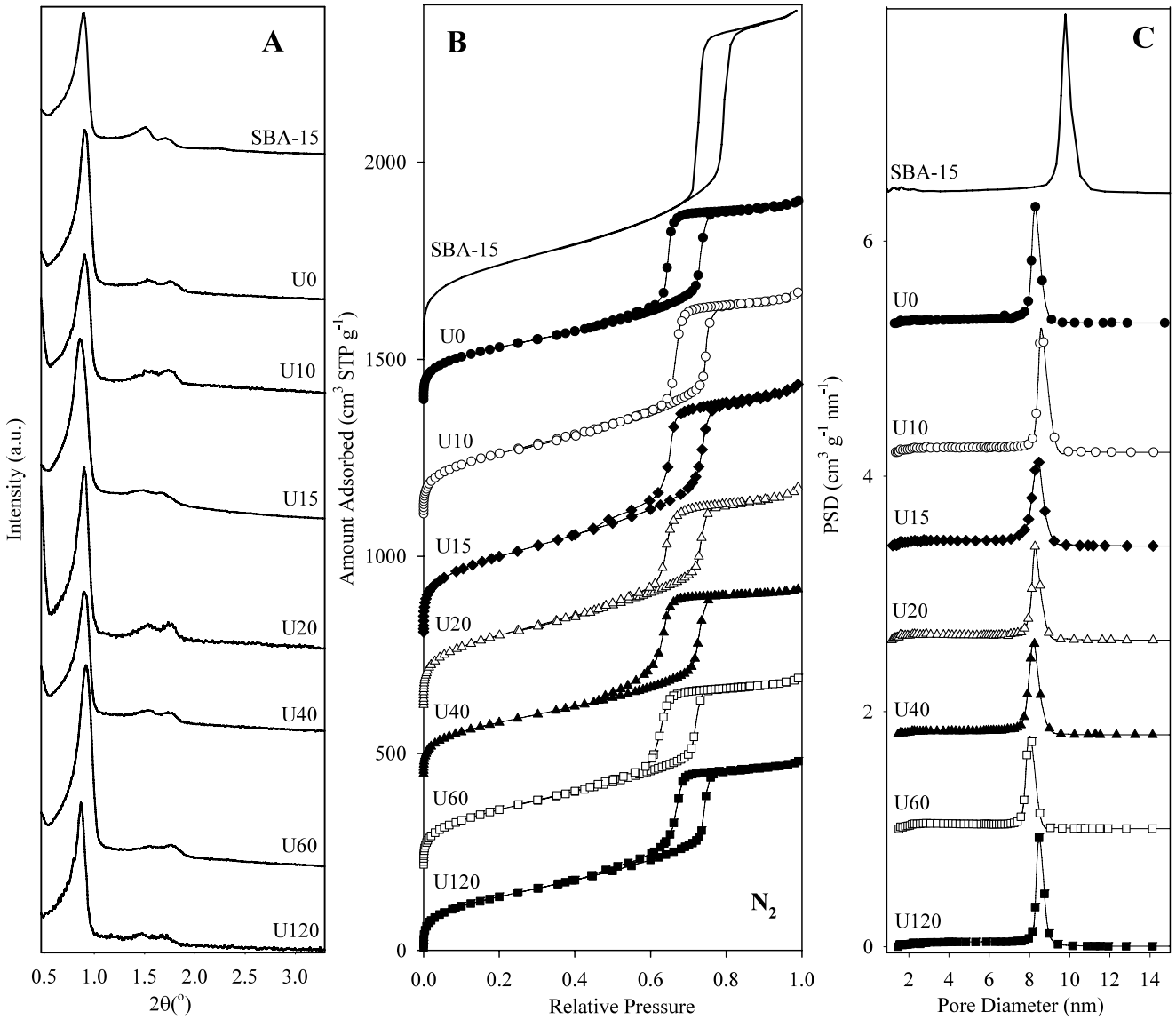

Fig. 1 X-ray diffraction (XRD) patterns (**A**), nitrogen adsorption isotherms (**B**) measured at −196 °C and the corresponding pore size distributions (PSDs) (**C**) calculated according to the improved KJS method (Jaroniec and Solovyov 2006) for the channel-like SBA-15 mesoporous silicas with ureidopropyl surface groups synthesized by delaying the addition of ureidopropyltrimethoxysilane (*U*) into the TEOS-polymer mixture from zero to 120 minutes; *numbers at the samples codes* denote the delay time in minutes. The adsorption isotherms and PSD curves for U60, U40, U20, U15, U10, U0 and SBA-15 were offset by 210, 440, 615, 800, 1100, 1390, 1500 cc STP g^{-1} and 1.0, 1.8, 2.6, 3.4, 4.2, 5.3, 6.4 cc g^{-1} nm^{-1}, respectively

meaningful changes in the XRD patterns, indicating that the structural quality of all samples studied is similar. Thus, a delay in adding the reactive organosilane into the TEOS-polymer gel mixture does not affect the structural ordering of the resulting OMOs.

The XRD patterns for both series of organosilicas (Figs. 1A and 2A) fulfill the relations for a 2D hexagonal structure (*p6m* symmetry group). These patterns exhibit one major peak indexed as (100) and two less intensive peaks indexed as (110) and (200). Since the OMO samples studied were obtained by employing the same block copolymer as that used for the synthesis of SBA-15 and their XRD patterns resemblance those for the SBA-15 mesostructured silicas, we will consider them as SBA-15 materials with incorporated ureidopropyl and disulfide groups, respectively.

3.2 Pore structure characterization

Shown in Figs. 1B, 2B and 1C, 2C are nitrogen adsorption-desorption isotherms measured at −196 °C for the extracted ureidopropyl-functionalized and disulfide-functionalized SBA-15 silicas and the corresponding pore size dis-

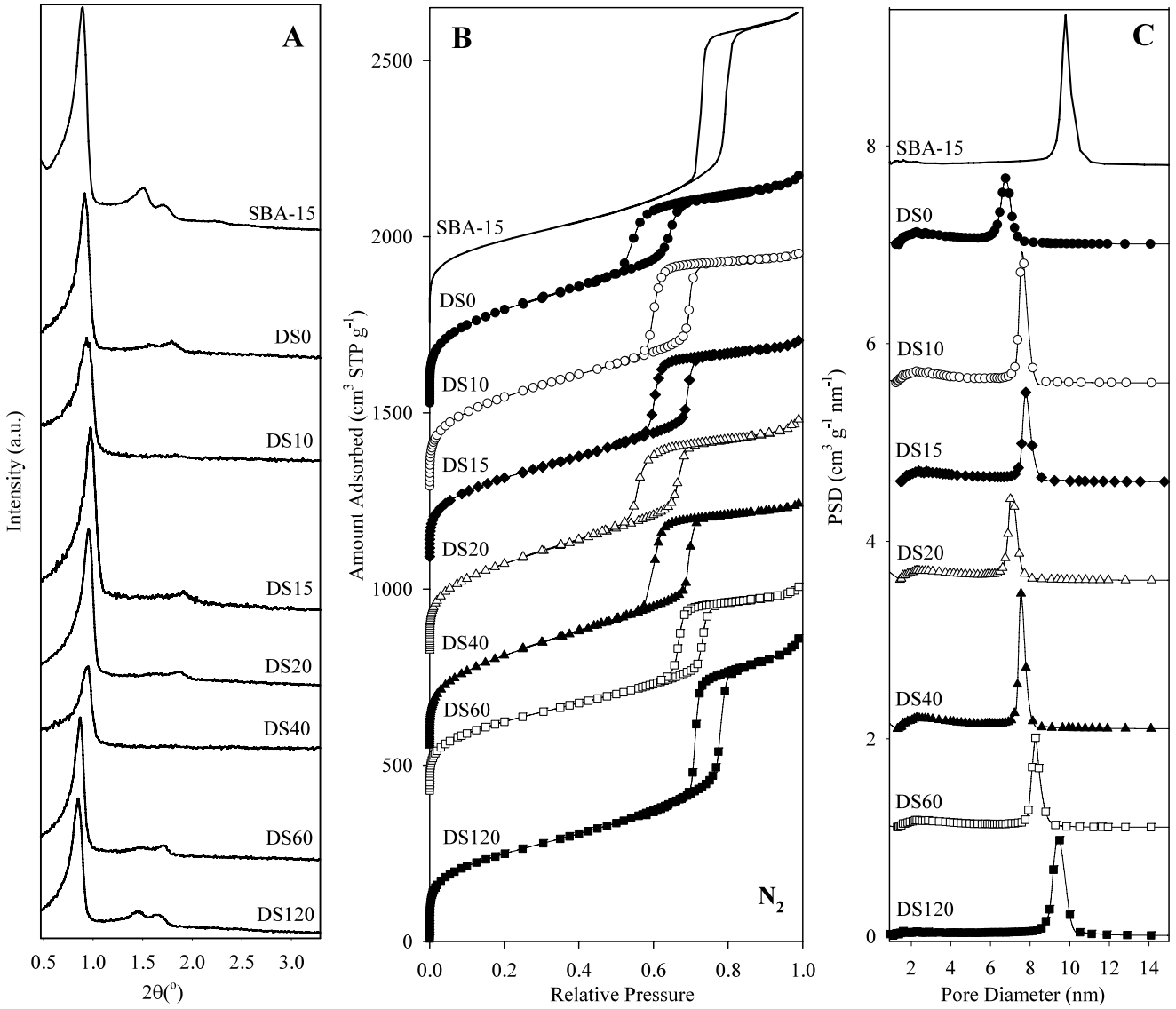

Fig. 2 X-ray diffraction (XRD) patterns (**A**), nitrogen adsorption isotherms (**B**) measured at −196 °C and the corresponding pore size distributions (PSDs) (**C**) calculated according to the improved KJS method (Jaroniec and Solovyov 2006) for the channel-like SBA-15 mesoporous silicas with disulfide bridging groups synthesized by delaying the addition of bis(triethoxysilylpropyl) disulfide (*DS*) into the TEOS-polymer mixture from zero to 120 minutes; *numbers at the samples codes* denote the delay time in minutes. The adsorption isotherms and PSD curves for DS60, DS40, DS20, DS15, DS10, DS0 and SBA-15 were offset by 420, 550, 820, 1080, 1280, 1520, 1750 cc STP g^{-1} and 1.1, 2.1, 3.6, 4.6, 5.6, 7.0, 7.8 cc g^{-1} nm^{-1}, respectively

tributions calculated from adsorption branches of the aforementioned isotherms by using the improved KJS (Kruk-Jaroniec-Sayari) method (Jaroniec and Solovyov 2006). In addition, these isotherms were used to obtain the BET specific surface area (Brunauer et al. 1938), the volume of complementary pores, the single-point pore volume (Sing et al. 1985) and the mesopore diameter, which are listed in Table 1. Similarly to unmodified SBA-15 silica, all extracted organosilicas exhibit type IV adsorption-desorption isotherms with a distinct H1 hysteresis loop typical for the materials with cylindrical mesopores. A comparison of the isotherms shown in Figs. 1B and 2B indicates that an increasing delay in the addition of reactive organosilane does not influence the shape of adsorption isotherms except for the SBA-15 sample with disulfide bridging groups, DS0, which was synthesized by adding TEOS and bis(triethoxysilylpropyl) disulfide at the same time. The pore size distributions (Figs. 1C and 2C) are narrow for all ureidopropyl- and disulfide-modified SBA-15 silicas except the DS0 sample. Moreover, the pore diameters do not change significantly for all ureidopropyl-modified SBA-15 samples, whereas for the samples with disulfide bridges there is a clear tendency of the pore size enlargement with increasing delay of organosilane addition.

The BET specific surface area for the OMOs studied is between 500–730 and 750–1000 $m^2\,g^{-1}$ for ureidopropyl- and disulfide-modified SBA-15 materials, respectively; thus, the values for the former series of OMOs, which have surface ligands are slightly lower than those for OMOs having organic groups incorporated into the framework. A similar trend is observed for a single-point volume, which is in the range from 0.76 to 0.99 cc g^{-1} as well as from 0.90 to 1.27 cc g^{-1} for ureidopropyl- and disulfide-modified SBA-15 silicas, respectively.

A comparison of the complementary pore volumes for both functionalized silicas obtained by integration of PSDs in the range of pore widths up to 4 nm reveals that these values are within ranges from 0.06 to 0.14 as well as from 0.12 to 0.26 cc/g for ureidopropyl- and disulfide-modified SBA-15 samples, respectively. It is noteworthy that these small pores originate from the penetration of hydrophilic ethylene oxide blocks into the siliceous walls. It can be noticed that higher values of the complementary pore volumes were acquired for the disulfide bridging spacers (see Table 1). In addition to ordered mesopores reflected by steep condensation steps, some of the isotherms such as those for U-15, U-20, U-60, DS-0, DS-15, DS-120 display the lack of plateau at higher relative pressures; their adsorption branch increases with pressure approaching the saturation vapor pressure, indicating the presence of secondary disordered mesopores also known as textural porosity.

4 Conclusions

Ureidopropyl- and disulfide-functionalized OMOs with *p6m* symmetry were prepared via co-condensation of TEOS and appropriate organosilane in the presence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) by gradually delaying the addition of reactive organosilane in relation to the TEOS addition. The XRD studies showed that all samples exhibited a long-range crystallographic ordering analogous to that in SBA-15 (*p6m* symmetry group), whereas adsorption analysis concluded that all materials possess uniform mesopores. This work shows that the time of addition of reactive organosilane to the synthesis gel does not play such a crucial role in the formation of organosilicas with both surface and bridging groups. However, the case of the DS0 sample suggests that the use of a short delay for the addition of organosilane (at least 15 min after TEOS addition) may be beneficial for the sample quality; this short delay is sufficient for the formation of the silica-polymer template mesostructure, which is flexible enough to accommodate organosilane units. A simultaneous addition of TEOS and organosilane precursors may disturb the formation of ordered structures. Thus, a delayed addition of reactive organosilane can be positive in achieving better uniformity of pores and pore openings.

Acknowledgements This work is based upon work supported by the National Science Foundation under Grants No. CTS-0553014 and CHE-0353737 (REU).

References

Abu-Lebdeh, Y.A.I., Budd, P.M., Nace, V.M.: Preparation of mesoporous silica with poly(oxyethylene)/(oxybutylene)/poly(oxyethylene) triblock copolymers as templates. J. Mater. Chem. **8**, 1839–1842 (1998)

Antochshuk, V., Jaroniec, M.: Simultaneous modification of mesopores and extraction of template molecules from MCM-41 with trialkylchlorosilanes, Chem. Commun., 2373–2374 (1999)

Antochshuk, V., Jaroniec, M.: Functionalized mesoporous materials obtained via interfacial reactions in self-assembled silica-surfactant systems. Chem. Mater. **12**, 2496–2501 (2000)

Asefa, T., MacLachlan, M.J., Coombos, N., Ozin, G.A.: Periodic mesoporous organosilicas with organic groups inside the channel walls. Nature **402**, 867–871 (1999)

Barrett, E.P., Joyner, L.G., Halenda, P.H.: The determination of pore volume and area distribution in porous substances. I. Computation from nitrogen adsorption. J. Am. Chem. Soc. **73**, 373–380 (1951)

Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., Schlenker, J.L.: A new family of mesoporous molecular-sieves prepared with liquid-crystal templates. J. Am. Chem. Soc. **114**, 10834–10843 (1992)

Brunauer, S., Emmet, P.H., Teller, E.: Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. **60**, 309–319 (1938)

Feng, X., Fryxell, G.E., Wang, L.Q., Kim, A.Y., Liu, J., Kemmer, K.: Functionalized monolayers on ordered mesoporous supports. Science **276**, 923–926 (1997)

Fulvio, P.F., Pikus, S., Jaroniec, M.: Tailoring properties of SBA-15 materials by controlling conditions of hydrothermal synthesis. J. Mater. Chem. **15**, 5049–5053 (2005)

Gong, Y.J., Li, Z.H., Wu, D., Sun, Y.H., Deng, F., Luo, Q., Yue, Y.: Synthesis and characterization of ureidopropyl-MSU-X silica. Microporous Mesoporous Mater. **49**, 95–102 (2001)

Grudzien, R.M., Jaroniec, M.: Cage-like ordered silica with large mesopore volume synthesized by doubling amount of polymer, adding sodium chloride and lowering acid concentration, Chem. Commun., 1076–1078 (2005)

Grudzien, R.M., Grabicka, B.E., Jaroniec, M.: Effective method for removal of polymeric template from SBA-16 silica combining extraction and temperature-controlled calcination . J. Mater. Chem. **16**, 819–823 (2006a)

Grudzien, R.M., Grabicka, B.E., Kozak, M., Pikus, S., Jaroniec, M.: Effect of polymer-to-silica ratio on the formation of large three-dimensional cage-like mesostructures. New J. Chem. **30**, 1071–1076 (2006b)

Grudzien, R.M., Grabicka, B.E., Pikus, S., Jaroniec, M.: Periodic mesoporous organosilicas with ethane and large isocyanurate bridging groups. Chem. Mater. **18**, 1722–1725 (2006c)

Grudzien, R.M., Grabicka, B.E., Jaroniec, M.: Adsorption and structural properties of channel-like and cage-like organosilicas. Adsorption **12**, 293–308 (2006d)

Grudzien, R.M., Pikus, S., Jaroniec, M.: Periodic mesoporous organosilicas with Im3m symmetry and large isocyanurate bridging groups. J. Phys. Chem. B **110**, 2972–2975 (2006e)

Hamoudi, S., Kaliaguine, S.: Sulfonic acid-functionalized periodic mesoporous organosilica. Microporous Mesoporous Mater. **59**, 195–204 (2003)

Hatton, B., Landskron, K., Whitnall, W., Perovic, D., Ozin, G.A.: Past, present, and future of periodic mesoporous organosilicas—the PMOs. Acc. Chem. Res. **38**, 305–312 (2005)

Hoffmann, F., Cornelius, M., Morell, J., Froba, M.: Periodic mesoporous organosilicas (PMOs): past, present, and future. J. Nanosci. Nanotechnol. **6**, 265–288 (2006)

Inagaki, S., Guan, S., Fukushima, Y., Ohsuna, T., Teresaki, O.: Novel mesoporous materials with a uniform distribution of organic groups and inorganic oxide in their frameworks. J. Am. Chem. Soc. **121**, 9611–9614 (1999)

Jaroniec, M.: Organosilica the conciliator. Nature **442**, 638–640 (2006)

Jaroniec, M., Solovyov, L.: Improvement of the Kruk-Jaroniec-Sayari method for pore size analysis of ordered silicas with cylindrical mesopores. Langmuir **22**, 6757–6760 (2006)

Jaroniec, C.P., Kruk, M., Jaroniec, M., Sayari, A.: Tailoring surface and structural properties of MCM-41 silicas by bonding organosilanes. J. Phys. Chem. B **102**, 5503–5510 (1998)

Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., Beck, J.S.: Ordered mesoporous molecular-sieves synthesized by a liquid-crystal template mechanism. Nature **359**, 710–712 (1992)

Kruk, M., Jaroniec, M., Sayari, A.: Application of large pore MCM-41 molecular sieves to improve pore size analysis using nitrogen adsorption measurements. Langmuir **13**, 6267–6273 (1997)

Kruk, M., Antochshuk, V., Matos, J.R., Mercuri, L.P., Jaroniec, M.: Determination and tailoring the pore entrance size in ordered silicas with cage-like mesoporous structures. J. Am. Chem. Soc. **124**, 768–769 (2002)

Lim, M.H., Stein, A.: Comparative studies of grafting and direct syntheses of inorganic-organic hybrid mesoporous materials. Chem. Mater. **11**, 3285–3295 (1999)

Lim, M.H., Blanford, C.F., Stein, A.: Synthesis and characterization of a reactive vinyl-functionalized MCM-41: Probing the internal pore structure by a bromination reaction. J. Am. Chem. Soc. **119**, 4090–4091 (1997)

Melde, B.J., Holland, B.T., Blandford, C.F., Stein, A.: Mesoporous sieves with unified hybrid inorganic/organic frameworks. Chem. Mater. **11**, 3302–3308 (1999)

Olkhovyk, O., Jaroniec, M.: Ordered mesoporous silicas with 2,5-dimercapto-1,3,4-thiadiazole ligand: High capacity adsorbents for mercury ions. Adsorption **11**, 205–214 (2005a)

Olkhovyk, O., Jaroniec, M.: Periodic mesoporous organosilica with large heterocyclic bridging groups. J. Am. Chem. Soc. **127**, 60–61 (2005b)

Sayari, A., Hamoudi, S.: Periodic mesoporous silica-based organic-ionorganic nanocomposite materials. Chem. Mater. **13**, 3151–3168 (2001)

Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniewska, T.: Reporting physisorption data for gas solid systems with special reference to determination of surface-area and porosity. Pure Appl. Chem. **57**, 603–619 (1985)

Taguchi, A., Schuth, F.: Ordered mesoporous materials in catalysis. Microporous Mesoporous Mater. **77**, 1–45 (2005)

Wang, X., Lin, K.S.K., Chan, J.C.C., Cheng, S.: Direct synthesis and catalytic applications of ordered large pore aminopropyl-functionalized SBA-15 mesoporous materials. J. Phys. B **109**, 1763–1769 (2005)

Zhao, D., Huo, Q., Feng, J., Chmelka, B.F., Stucky, G.D.: Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. J. Am. Chem. Soc. **120**, 6024–6036 (1998)