

Surface Modifications of Cage-like and Channel-like Mesopores and Their Implications for Evaluation of Sizes of Entrances to Cage-like Mesopores

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Received: March 15, 2003; In Final Form: August 24, 2003

In our recent brief communication, we have proposed a new method for the evaluation of the pore entrance size in silicas and other materials with cage-like mesopores. This method is based on the modification of the material with ligands that are capable of forming a dense monolayer chemically bonded on the surface. The size of the smallest ligand that is capable of rendering the cage-like pores inaccessible for gas molecules is related to the pore entrance size. In the case of silicas, this method allows one to readily evaluate pore entrance diameters between about 1 and 5 nm. Herein, details of this novel approach are reported. It is shown that the introduction of the surface ligands can be monitored using thermogravimetric analysis under air, whereas the elemental analysis does not allow one to differentiate between carbon contents from chemically bonded ligands and trapped organic species. The surface modification inherently leads to the adsorption capacity loss, which depends on the pore diameter, amount of framework micropores, and surface modifier loading. It is suggested how to distinguish the adsorption capacity loss related to the pore blocking from that merely resulting from the surface groups introduction. Differences in the pore blocking behavior for cage-like pores and channel-like pores are demonstrated. Unprecedented, one-step micropore filling with nitrogen at relatively high pressures is reported for a material with narrow cylindrical pores with a hydrophobic surface. This work provides a solid foundation for the use of the surface modification method in the elucidation of the pore entrance size.

1. Introduction

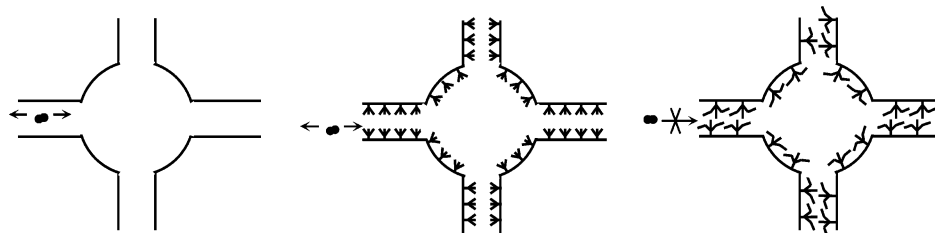
Over the past 9 years, there has been a significant interest in the synthesis,^{1–22} characterization,^{13,17,22–29} and application^{11,30–39} of ordered silicas with cage-like mesoporous structures (OSCMSs). OSCMSs can be synthesized using alkylammonium surfactants^{1,2} and oligomeric or block copolymeric templates.⁵ Because of their 3-dimensional, multidirectional pore connectivity, OSCMSs and their functionalized derivatives may find applications as catalysts,^{11,30–33} sensors,³⁴ thin films,^{3,4,8,9} adsorbents,³⁵ molecular sieves,^{20,25} hosts for biomolecules^{36,37} and quantum dots,³⁸ and templates for the nanostructures synthesis.^{39,40}

One of the important structural features of OSCMSs is that their pore (cage) diameter is usually much larger than the pore entrance diameter. Relatively little work have been reported on the evaluation of the pore entrance sizes in OSCMSs.^{13,20,24,25} First estimates of OSCMS pore entrance size were obtained using the electron crystallography for SBA-1¹ and SBA-6 silicas of cubic *Pm3n* structure and for SBA-16 silica⁵ of cubic *Im3m* structure.¹³ However, the powerful electron crystallography method appears to be applicable only for highly ordered materials with sufficiently large sizes of ordered domains. Moreover, this method requires expensive transmission electron microscopy (TEM) instrumentation and an extensive TEM imaging of the material from different directions, which makes it impractical for a routine use. Later, we proposed that the OSCMS pore entrance size can be evaluated on the basis of the pore accessibility after the surface modification with monolayers of ligands of different sizes (see Scheme 1).²⁵ This novel method is complementary to the electron crystallography

because it is applicable not only for highly ordered materials but also for less ordered or even disordered materials with cage-like pores and can be used for a routine analysis. However, the introduction of a dense monolayer of groups of well-defined size can be conveniently performed primarily for materials with silica-based or organosilica-based surfaces and may be less practical for materials with many other compositions, unlike the electron crystallography that is potentially applicable for 3-dimensionally ordered materials with any framework composition. The method based on the surface modification is applicable for pore entrance sizes somewhere between 1 and 5 nm.²⁵

The work on surface modification of OSCMSs showed the potential of the use of these materials as molecular sieves because it was observed that small changes in the size of surface ligands can dramatically change the pore accessibility.²⁵ In particular, an OSCMS sample, whose pores were accessible to nitrogen at 77 K after the surface modification with trimethylsilyl (TMS) ligands, exhibited largely inaccessible pore structure after the modification with triethylsilyl (TES) ligands which are capable of additionally reducing the pore diameter by only about 0.25 nm. These results showed that the pore entrance in the considered OSCMS sample was about 1.3 nm in diameter (as estimated from the size of the TMS ligand and the dimensions of nitrogen molecule),²⁵ whereas the pore entrance size in the TMS-modified OSCMS was below 0.6 nm; otherwise, TES ligands would not be large enough to block the access of nitrogen molecules (size of about 0.35 nm) to the cage-like pores. These results were highly promising as far as the synthesis of OSCMS molecular sieves is concerned. Very recently, molecular sieving properties of OSCMSs were actually demonstrated using nitrogen, cyclopentane, and mesitylene as

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SCHEME 1: Changes in Accessibility of Cage-like Pores as a Result of the Introduction of a Layer of Surface Ligands (Taken from Ref 25)

adsorbates.²⁰ The use of molecules of different sizes obviously opens another way for the estimation of the OSCMS pore entrance size,²⁰ which is practical primarily for entrances of size comparable to that of molecules that can be conveniently used for such studies, whose dimensions are below 1 nm. The analysis of desorption branches of adsorption–desorption hysteresis loops emerges as another convenient method for the pore entrance diameter assessment, although it is so far restricted to diameters above about 4 nm.^{27,29} Therefore, the pore entrance size range from about 1 to 4 nm can be effectively probed only by using the electron crystallography¹³ (for materials with sufficiently large sizes of highly ordered domains) and the method based on the monitoring of pore accessibility after the surface modification.²⁵

The ability to assess the pore entrance size in OSCMSs is a starting point for the identification and/or elaboration of synthesis approaches for the pore entrance size control. The electron crystallography characterization revealed that the use of different surfactant templates is capable of providing materials with the same structure, but different entrance size.¹³ Our work on the pore entrance size assessment using the surface modification method provided foundations for a more convenient pore entrance diameter control via the synthesis temperature and time adjustment without the need of changing the copolymeric template type.²⁵ The issue of the pore entrance size tailoring through the synthesis temperature and time control was further explored in subsequent studies.^{21,22} The synthesis time control was also found effective⁴¹ in the preparation of silica mesocellular foams (MCFs),⁴² which are large-pore materials with quite uniform pore diameter, but often with appreciably disordered structures. This way of structural tailoring is clearly advantageous over the previously known methodology involving the use of latex templates prepared under appropriate conditions.⁴³ It was demonstrated that the change in the synthesis conditions, such as pH, in the OSCMS synthesis can also modify the pore window diameter obtained for the same kind of surfactant template.²⁰

The present work is a complete account of our research on a novel method of the pore entrance size assessment through the monitoring of the pore accessibility after the surface modification, which we reported earlier in a brief communication.²⁵ Herein, the details of the surface modification procedure are provided, the use of thermogravimetry and elemental analysis to evaluate the bonded group loading is discussed, and the dependence of adsorption properties on the degree of pore blocking is highlighted.

2. Materials and Methods

2.1. Materials. FDU-1 silicas were synthesized from tetraethyl orthosilicate (TEOS) in the presence of the poly(ethylene oxide)–poly(butylene oxide)–poly(ethylene oxide) triblock copolymer template (B50-6600 from Dow) under acidic conditions, as originally proposed by Zhao et al.¹⁵ The details of the

synthesis procedure employed herein were reported elsewhere.^{17,22} Two FDU-1 silicas were used for the present study: one synthesized at room temperature (about 303 K) (sample I) and the other one synthesized initially at room temperature (about 298 K) and subjected to a hydrothermal treatment at 373 K (sample II). Results of detailed structural characterization of these samples (denoted T303 and T298H373-6h2) using transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), powder X-ray diffraction (XRD), and nitrogen adsorption can be found elsewhere.²² MCM-41 (2.4), (3.1), and (3.5) silicas (numbers in parentheses provide the pore diameter in nanometers) were synthesized and characterized as reported elsewhere (samples were denoted C8-H, C12, and C14).^{45,46}

The ordered mesoporous silicas were modified with organosilyl ligands in a way similar to that employed in our earlier work.⁴⁷ About 0.1 g of the calcined silica sample was dispersed in 2.5 mL of the silane and 15 mL of pyridine. The mixture was refluxed for 1 day (temperature about 393 K). After cooling, the resultant sample was washed repeatedly on a glass filter with small portions of toluene, isopropyl alcohol, and heptane. Subsequently, the sample was dried overnight in a vacuum oven at 368–373 K. The silanes used for the surface modification include trimethylchlorosilane, triethylchlorosilane, propyldimethylchlorosilane, butyldimethylchlorosilane, hexyldimethylchlorosilane, octyldimethylchlorosilane, and decyldimethylchlorosilane. The corresponding alkylsilyl ligands are denoted TMS, TES, PDMS, BDMS, HDMS, ODMS, and DDMS. The modified samples are denoted using the notation for the unmodified silica and the notation for the ligand. For instance, I-ODMS denotes ODMS-modified FDU-1 sample I.

2.2. Measurements. Weight change patterns were recorded under an air atmosphere on a TA Instruments TGA 2950 high-resolution thermogravimetric analyzer in a high-resolution mode with the maximum heating rate of 5 K min⁻¹. The carbon content was evaluated using a LECO CHNS-932 elemental analyzer. Nitrogen adsorption isotherms were measured on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the adsorption measurements, the samples were outgassed under vacuum for 2 h or more at 473 K (for unmodified silicas) or 383 K (for modified silicas).

2.3. Calculations. The BET specific surface area was calculated from adsorption data in the relative pressure range from 0.04 to 0.2.⁴⁸ In the case of MCM-41 (2.4) and (3.1) samples, data for somewhat lower relative pressures (0.01–0.02 and 0.04–0.1 intervals, respectively) were used. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.99.⁴⁸ The pore size distributions (PSDs) were evaluated using methods calibrated for cylindrical pores⁴⁹ and with statistical film thickness curves (*t*-curves) suitable for materials with siliceous surfaces^{49,50} or with highly hydrophobic surfaces.⁵¹ The *t*-curve for silica surface⁵⁰ was used in calculations for unmodified samples and the sample modified

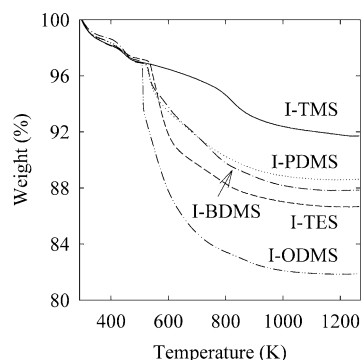


Figure 1. Weight change curves for FDU-1 silica synthesized at room temperature and modified with different organosilyl ligands.

with trimethylsilyl ligands. In cases of other modified samples, the t-curve for a highly hydrophobic surface⁵¹ was used. In the case of FDU-1 silica with spherical pores, the method employed in PSD calculations is expected to systematically underestimate the pore diameter by about 2 nm because of the fact that this method was calibrated for a different geometry (that is, cylindrical).²²

3. Results and Discussion

3.1. Thermogravimetry and Elemental Analysis. An important step in the evaluation of the pore entrance diameter through the surface-modification/pore-accessibility-determination approach is to ensure that the surface modification was successfully performed, that is, that a dense monolayer of surface ligands was introduced. The formation of a monolayer rather than a multilayer⁵² of ligands can be ensured by using monofunctional organosilanes (for instance, monochlorosilanes used in the present study) that are not capable of polymerizing and forming multilayers on the pore surface, in contrast to bi- or trifunctional organosilanes. On the other hand, the amount of the surface ligands introduced can be determined using either elemental analysis or thermogravimetry (TGA). In the case of the modification with organosilanes, the elemental analysis is capable of providing the carbon content in the modified material, which allows one to evaluate the coverage of the bonded groups. However, one needs to keep in mind that the surface coverage determined this way may be overestimated because a certain percentage of the carbon content may come from the residual unreacted silane or other organics introduced during the modification or washing. TGA allows one to measure weight loss with temperature and thus requires a careful data interpretation in order to evaluate the bonded group content. In particular, it is important to ensure that the final composition of the sample after heating is known. For instance, dehydroxylated silica (SiO_2) can be assumed to be the primary product of the heating of organosilane-functionalized silica under air up to about 1270 K, whereas the product of the heating under nitrogen is difficult to ascertain, as it may contain carbon residue and some silica species of ill-defined structure. Although the elucidation of quantitative information from TGA data is somewhat speculative even if proper conditions are chosen (unless the TGA assessment is confirmed using an independent, direct technique), TGA may allow one to discriminate between chemically bonded groups and species that are physisorbed or trapped in the pores. The latter feature is an important advantage of the TGA analysis of silicas chemically modified with organosilanes.

Shown in Figures 1 and 2 are weight change patterns under air recorded for FDU-1 silicas modified with different organosilanes. The weight loss below about 373 K can be attributed

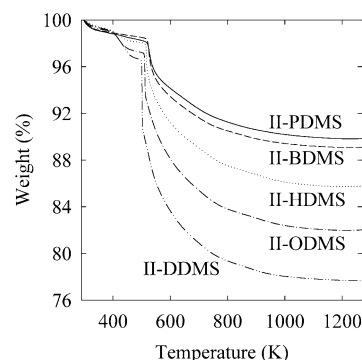


Figure 2. Weight change curves for FDU-1 silica synthesized by employing a postsynthesis hydrothermal treatment at 373 K and modified with different organosilyl ligands.

to thermodesorption of physically adsorbed water or solvents used for modification or washing. The main weight loss related to the decomposition of the bonded groups was observed above 473 K. The magnitude of this weight loss tended to systematically increase as the number of carbon atoms in the organosilane ligand increased. This indicates that for the FDU-1 samples considered herein the surface modification was successfully accomplished for all the organosilanes used, independent of their size and structure. Some of the weight change patterns featured a distinct weight loss event between 373 and 473 K. This event was observed primarily for samples, whose pores were inaccessible to nitrogen at 77 K (see below), and therefore can be attributed to species that were trapped in the blocked cage-like pores and were not able to exit the porous structures at lower temperature. It is interesting to note that the amount of the trapped species was relatively low, despite the fact that one would expect a significant amount of the modifier or solvent enclosed in the pores after the modification. If this is actually the case, the TGA data indicate that most of these species can leave the pores during the washing at room temperature or drying at 368–373 K.

The above discussion suggested that weight change patterns recorded under air provide valuable information about the amount of the chemically bonded ligands. This contention was confirmed by comparing the TGA data with the elemental analysis results. Carbon contents in the modified samples were used to evaluate the weight of the bonded ligands per gram of the sample and to predict the weight loss that would correspond to the oxidative removal of the organic groups (temperature range from about 500 to 1270 K). It was assumed that in the considered temperature range $-\text{OSiR}_1\text{R}_2\text{R}_3$ ligands (R_1 , R_2 , and R_3 are alkyl groups) are transformed into $-\text{OSiO}_{1.5}$ structural units and that silica is not otherwise dehydroxylated. Under these assumptions, the recorded weight losses for the modified samples were highly consistent with the weight losses predicted on the basis of the loadings of the surface groups evaluated on the basis of the elemental analysis. It can be concluded that weight change curves recorded under an air atmosphere provide reliable information about the organosilane group content in modified materials. The ligand loadings per gram and per square meter of unmodified silica are listed in Tables 1 and 2. These loadings were in most cases assessed on the basis of % C from elemental analysis, although in some cases where % C was not determined, TGA data were used to estimate the loadings. It can be seen that the loading of the surface groups tended to decrease as the size of the groups increased. The only major exception from this behavior was the case of the TES ligands, whose surface coverage was relatively very high. It should be noted that the surface coverages attained for FDU-1 samples

TABLE 1: Properties of Unmodified and Modified FDU-1 Samples

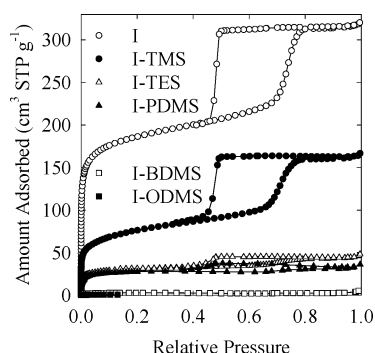
sample	BET specific surface area (m ² g ⁻¹)	total pore volume (cm ³ g ⁻¹)	pore diameter ^a (nm)	ligand loading ^b (mmol g ⁻¹)	surface coverage ^b (μmol m ⁻²)
I	650 ^c	0.49 ^c	9.0 ^c (10.6) ^{c,d}	N/A	N/A
I-TMS	270	0.25	8.2	1.57 ^e	2.43 ^e
I-TES	110	0.07	7.7	1.81 ^e	2.80 ^e
I-PDMS	100	0.06	<i>f</i>	1.46 ^e	2.26 ^e
I-BDMS	~10	<0.01	<i>f</i>	1.33 ^e	2.06 ^e
I-ODMS	<10	<0.01	<i>f</i>	1.37 ^e	2.12 ^e
II	820 ^c	0.68 ^c	10.6 ^c (12.0) ^{c,d}	N/A	N/A
II-PDMS	330	0.36	9.7	1.98	2.42
II-BDMS	280	0.32	9.5	1.79	2.19
II-HDMS	80	0.12	9.3	1.7 ^{e,g}	2.1 ^{e,g}
II-ODMS	<10	<0.01	<i>f</i>	1.58 ^e	1.93 ^e

^a Pore diameter estimated under assumption of cylindrical pore geometry. The actual pore size is expected to be about 1–2 nm larger. ^b Quantities per 1 g or 1 m² of the FDU-1 silica support, evaluated on the basis of % C from elemental analysis. ^c Taken from ref 22. ^d Evaluated in ref 22 using the geometrical equation (reported in ref 26). ^e May be overestimated, as % C may include contribution from organic species that are not chemically bonded. ^f Too small adsorption capacity; adsorption data not reliable enough to determine the pore size. ^g Estimated from TGA.

TABLE 2: Properties of Unmodified and Modified MCM-41 Samples

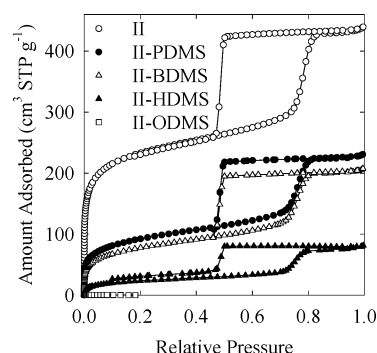
sample	BET specific surface area (m ² g ⁻¹)	total pore volume (cm ³ g ⁻¹)	pore diameter (nm)	ligand loading ^a (mmol g ⁻¹)	surface coverage ^a (μmol m ⁻²)
(2.4)	850 ^b	0.54 ^b	2.4 ^b	N/A	N/A
(2.4)-BDMS	260	0.13	1.0	2.32	2.74
(2.4)-HDMS	<10	<0.01	<i>c</i>	1.6 ^d	1.9 ^d
(2.4)-ODMS	<10	<0.01	<i>c</i>	1.38	1.63
(3.1)	950 ^e	0.66 ^e	3.1 ^e	N/A	N/A
(3.1)-ODMS	~130	0.08	<i>f</i>	2.02	2.13
(3.5)	1020 ^e	0.79 ^e	3.5 ^e	N/A	N/A
(3.5)-ODMS	~310	0.16	<i>f</i>	2.3 ^d	2.2 ^d

^a Quantities per 1 g or 1 m² of the MCM-41 silica support, evaluated on the basis of % C from elemental analysis. ^b Taken from ref 45. ^c Too small adsorption capacity; adsorption data not reliable enough to determine the pore size. ^d Estimated from TGA. ^e Taken from ref 46. ^f Could not be determined with reasonable accuracy because of very slow equilibration at low pressures during adsorption measurements.

**Figure 3.** Nitrogen adsorption isotherms for FDU-1 silica synthesized at room temperature, unmodified and modified with different ligands (data taken from ref 25).

were relatively high in all cases (compare for instance with coverages reported in refs 47 and 53). Actually, the surface coverages for FDU-1 silicas were remarkably high, when one takes into consideration that an appreciable part of the FDU-1 surface area is constituted by the surface area of micropores (in the silica framework). The micropores may not be readily accessible to the organosilane surface modifier, and the surface coverage in them is likely to be relatively low. This argument would suggest that the coverage of ligands on the surfaces of ordered mesopores and entrances to them is very high in the case of FDU-1 modified as described herein.

3.2. Nitrogen Adsorption. Nitrogen adsorption isotherms for organosilane-modified FDU-1 silicas are shown in Figures 3 and 4. These adsorption isotherms have already been reported in our communication.²⁵ In the case of FDU-1 sample I, the modification with TMS ligands led to a significant decrease of the adsorption capacity. The decrease in adsorption capacity (per unit mass of the sample) after the surface modification is

**Figure 4.** Nitrogen adsorption isotherms for FDU-1 silica synthesized by employing a postsynthesis hydrothermal treatment at 373 K, unmodified and modified with different organosilyl ligands (data taken from ref 25).

expected because the surface groups introduced increase the mass of the sample and occupy a part of the pore volume. Moreover, in the case of polymeric-templated silicas, there is an additional cause of the decrease in adsorption capacity related to the presence of micropores in the frameworks of these silicas (a typical feature of these materials^{47,54}). The framework micropores appear to be partially or fully inaccessible as a result of the modification with organosilanes.^{47,54} The comparison of the adsorption capacity decrease for TMS-modified FDU-1 and SBA-15 silicas (SBA-15 silica⁵ exhibits a 2-D hexagonally ordered array of cylindrical mesopores separated from one another by typically microporous walls)^{47,54} indicates that the above factors (that is, the factors not related to the blocking of mesopores) are primarily responsible for decrease in adsorption capacity observed for TMS-modified FDU-1 sample I. On the other hand, in the case of the modification of FDU-1 sample I by triethylsilyl ligands, not only these three factors but also a

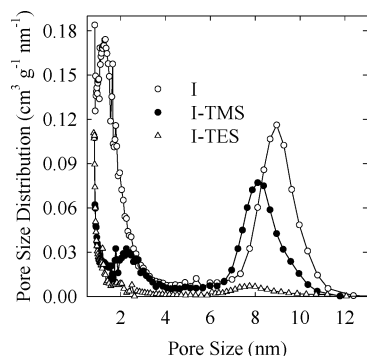


Figure 5. Pore size distributions for FDU-1 silica synthesized at room temperature, unmodified and modified with TMS and TES ligands.

prominent blocking of ordered mesopores was observed. This can be inferred from a drastic reduction of the height of the capillary condensation step after the modification. The examination of PSDs for the unmodified FDU-1 silica I and the TMS and TES-modified samples (Figure 5) leads to the same conclusion. In the case of the modification with the smaller ligand (TMS), the height of the PSD peak somewhat decreased, whereas in the case of the modification with the larger ligand (TES), there was only a weak PSD peak corresponding to the accessible uniform mesopores. FDU-1 sample I modified with PDMS, BDMS, and ODMS ligands exhibited even a more pronounced pore blocking, so much so that the latter two samples exhibited essentially no nitrogen adsorption (see Figure 3). On the basis of these results and taking into account the size of the organosilyl ligands and nitrogen molecules, the pore entrance size in FDU-1 sample I was assessed to be primarily above ~ 1.2 nm, but mostly below ~ 1.4 nm, and exclusively below ~ 1.9 nm.²⁵ Therefore, an average pore entrance size in this sample was about ~ 1.3 nm. This was almost by an order of magnitude smaller than the pore cage diameter, which was about 10.6 nm, as estimated from SAXS interplanar spacing data and pore volume²² using a geometrical equation proposed in ref 26. It should be noted that although the PSD peak for this sample was centered at 9.0 nm (see Figure 5), the calculation method used was calibrated for cylindrical pores, and therefore it underestimates the size of spherical pores, as noted elsewhere.^{17,22} On the basis of the above results, it is clear that it is possible to synthesize OSCMSs with relatively very narrow pore entrances.

In the case of FDU-1 sample II, the introduction of PDMS and BDMS ligands decreased the adsorption capacity, as expected (see Figure 4), but it did not appear to lead to any appreciable blockage of ordered mesopores (see PSDs in Figure 6). On the other hand, the introduction of somewhat larger HDMS ligands led to a more significant drop in the adsorption capacity and a marked decrease in the height of the PSD peak. Moreover, the adsorption isotherm for the HDMS-modified FDU-1 clearly exhibited low-pressure hysteresis. Apparently, the diffusion of nitrogen through the porous structure of this material was restricted to some extent and significantly slowed down. The observed significant drop in the adsorption capacity and the poor transport properties in the porous network of the II-HDMS sample indicate that the cage-like pores of this sample were partially made inaccessible by the surface modifier. This is also consistent with the fact that the ODMS-modified sample II exhibited essentially no nitrogen uptake. These results allowed us to estimate that the pore entrance size of this material is primarily above 1.9 nm, but exclusively below 2.9 nm, and that the average pore entrance size is about 2.4 nm.²⁵

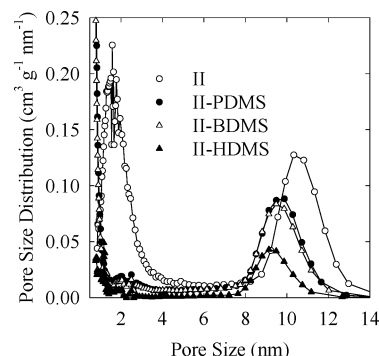


Figure 6. Pore size distributions for FDU-1 silica synthesized by employing a postsynthesis hydrothermal treatment at 373 K, unmodified and modified with PDMS, BDMS, and HDMS ligands.

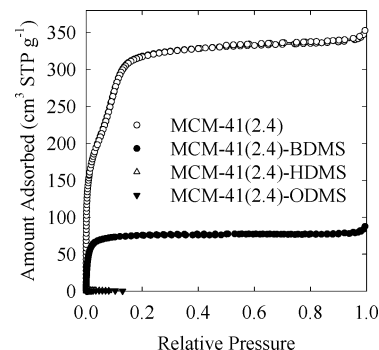


Figure 7. Nitrogen adsorption isotherms for MCM-41 silica (pore diameter 2.4 nm) unmodified and modified with BDMS, HDMS, and ODMS ligands (data for MCM-41 taken from ref 45).

The above estimates of the pore entrance size were based on an assumption that alkyl chains of the ligands that cause the pore inaccessibility are fully extended vertically from the surface. Earlier studies of surface modification of pores of diameter much larger than the size of the fully extended surface modifier indicated that the long-chain alkyls in alkylsilyl ligands are not fully extended⁵³ because the pore radius decrease after the surface modification was significantly smaller than the maximum length of the ligand with fully extended alkyl group. However, in the case of pores of radius comparable to the maximum size of the extended ligand, a different behavior is possible. To verify whether the ability of a given ligand to block the constrictions of a given diameter can be judged on the basis of the length of the ligand in the fully extended conformation, surface modifications of MCM-41 silicas with pore diameters of 2.4, 3.1, and 3.5 nm were performed.²⁵ Nitrogen adsorption isotherms for the unmodified and modified MCM-41 samples are shown in Figures 7 and 8. It can be seen that the modification of MCM-41(2.4) with BDMS ligands, which are capable of decreasing the pore diameter by not more than 1.5 nm, resulted in a significant decrease in the adsorption capacity and pore diameter (to about 1.0 nm) (see Table 2), but the pores were still accessible to nitrogen molecules (size of about 0.35 nm). On the other hand, the pores of MCM-41(2.4) were no longer accessible to nitrogen after the introduction of HDMS and ODMS ligands that are capable of decreasing the pore diameter by up to 2.0 and 2.5 nm, respectively. This result strongly suggests that, in the case of organosilyl groups with long-chain alkyls, at least some of these alkyl chains can in fact attain fully extended conformations, which leads to the pore blockage when the length of the fully extended ligand approaches the pore radius. It was also found that ODMS ligands are not capable of blocking the access of nitrogen to the MCM-41 pores of

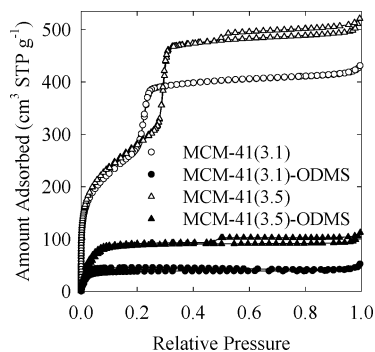


Figure 8. Nitrogen adsorption isotherms for MCM-41 silicas (pore diameters 3.1 and 3.5 nm), unmodified and modified with ODMS ligands (data for MCM-41 taken from ref 46).

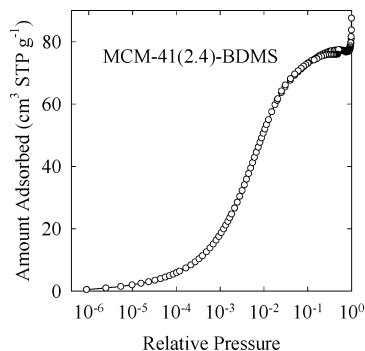


Figure 9. Low-pressure nitrogen adsorption isotherm for MCM-41 silica (pore diameter 2.4 nm) modified with BDMS ligands.

diameters of 3.1 and 3.5 nm, as expected from the fact that the surface modification with these groups can decrease the pore diameter by not more than 2.5 nm, leaving at least 0.6 nm void, which is large enough for nitrogen molecules to enter. However, the equilibration during adsorption measurements on these modified samples (MCM-41(3.1)-ODMS and MCM-41(3.5)-ODMS) was very slow, and it was not possible to reliably acquire adsorption data below the relative pressure of about 0.01. In contrast, it was possible to acquire well-equilibrated low-pressure nitrogen adsorption data for MCM-41(2.4)-BDMS sample (see Figure 9). This material exhibited an unusual adsorption behavior because it adsorbed only a small amount of gas at relative pressures below about 10^{-3} , which was followed by a one-step micropore filling primarily in the relative pressure range from 10^{-3} to 0.02. The one-step micropore filling of nitrogen is usually observed at much lower relative pressures (see results reported in refs 55 and 56). However, in the case of a material with a highly hydrophobic surface (for instance, silica with high surface coverage of BDMS groups),⁵³ the low-pressure nitrogen adsorption tends to be very low, and the statistical monolayer on the pore surface is formed at relative pressures much higher⁵¹ than in the case of silicas⁵¹ or carbons.⁵⁵ This may lead to the micropore filling at rather high relative pressures. Perhaps the one-step filling observed for MCM-41(2.4)-BDMS is a combination of the monolayer formation and the filling of the remaining pore space, despite the fact that in uniform pores these two events usually take place at somewhat different pressures.

The above results demonstrate that organosilanes with long-chain alkyl groups can attain fully extended conformation of the alkyl chain in pores, whose radius is close to the length of the fully extended group.²⁵ Our results also show that, in cases of the introduction of high coverages of relatively large groups on surfaces of narrow cylindrical pores, the decrease in adsorption capacity is very significant even if the pores are still

accessible. This is primarily because of the fact that densely bonded large groups occupy a significant fraction of space in a narrow cylindrical pore. Therefore, in cases where materials with narrow cylindrical pores are modified, leading to a significant, although not complete, loss of adsorption capacity, it may be difficult to ascertain whether this adsorption capacity loss is caused by some degree of pore blocking or merely by the prominent decrease in the volume of void space in the pores and increase of the mass of the sample.

3.3. Applicability of the Discussed Method. The pore entrance size assessment through the monitoring of pore accessibility after the surface modification with ligands of different sizes is expected to be suitable for the characterization of various OSCMSs reported in the literature.^{1–23} In addition, this method is applicable for disordered silicas with cage-like pores as well as for silica mesocellular foams with narrow pore windows.^{41,43} Moreover, ordered silicas with channel-like pores with constrictions, such as plugged hexagonal templated silicas,^{57–59} can be characterized using the approach discussed herein. The applicability of the proposed method does not appear to be restricted to silicas. For instance, periodic mesoporous organosilicas (PMOs), which are silicas with organic groups integrated in their frameworks,^{60–62} are also amenable to the surface modification with organosilanes, and thus the proposed method is expected to be suitable for characterization of these remarkable novel mesoporous materials.

4. Conclusions

The evaluation of the pore entrance diameter through the chemical modification of the surface of the material using organosilanes and the determination of the accessibility of the pore structure after the modification is a new, convenient approach for the characterization of silicas with cage-like pores. Organomonochlorosilanes were found to be suitable for this purpose. In the case of the modification procedure employed, the amount of the chemically bonded organosilane indicated that the modification proceeds uniformly on the surface of cage-like pores as well as on the surface of entrances to these pores. Even in cases where the modifier eventually blocked access to the cage-like pores, there was no evidence that the modification was restricted only to the external parts of particles of the material. Although there was some evidence that a certain amount of unreacted modifier can be trapped in the blocked pores, this amount was found to be relatively small. Thermogravimetry was found very useful in distinguishing between the chemically bonded and trapped species and was suitable for the estimation of the coverage of bonded groups. Nitrogen adsorption is a convenient method to determine the accessibility of the cage-like pores after the surface modification, but it needs to be kept in mind that the surface modification itself may bring a major decrease in adsorption capacity even if the pore blocking by the modifier does not occur. The occurrence of low-pressure hysteresis may be an indication of a partial pore blocking. Organic-modified narrow pores may exhibit peculiar adsorption properties, such as a one-step micropore filling at relatively high pressures.

Acknowledgment. M.J. acknowledges support by NSF Grant CHE-0093707. Dr. Jivaldo R. Matos (University of Sao Paulo, Brazil) is gratefully acknowledged for the synthesis of FDU-1 samples used for the modification. The authors thank Dr. Rene Geiger from Dow Chemicals for providing the triblock copolymer.

References and Notes

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