Tailoring Surface and Structural Properties of MCM-41 Silicas by Bonding Organosilanes

C. P. Jaroniec,[†] **M. Kruk, and M. Jaroniec***

Department of Chemistry, Kent State University, Kent, Ohio 44242

A. Sayari

Department of Chemical Engineering and CERPIC, Universite Laval, Ste-Foy, Qc, Canada G1K 7P4

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Large pore MCM-41 silica with the pore diameter of 5.0 nm was chemically modified by bonding monomeric-type ligands, such as trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl, as well as polymeric-type 3-aminopropylsilyl, (hexanoyl-3-aminopropyl)silyl, and octylsilyl ligands. The obtained materials were characterized using elemental analysis, high-resolution thermogravimetry (TGA), and nitrogen adsorption at 77 K in a wide range of pressures. Surface coverages of bonded ligands were between 2.5 and 3.0 μmol/m^2. It was shown that pore diameters of the samples studied decreased systematically with the increase in size of ligands. The modified materials exhibited narrow and monodisperse pore size distributions, indicating that the chemical bonding procedure did not diminish the structural ordering of the MCM-41 support. TGA data showed that the surface affinity to water was strongly dependent on the structure and functionality of the bonded species. Nitrogen adsorption data provided additional information about surface properties of the materials. A significant decrease in the amount of nitrogen adsorbed at low pressures was observed for the modified samples, especially those with long-chain alkyl groups. Low-pressure adsorption data were used to calculate adsorption energy distributions (AEDs), and peaks on these distributions were assigned to certain groups present on the silica surface or in the structure of bonded phases. It was thus demonstrated that the pore size and surface functionality of ordered mesoporous silicas can be engineered by a proper choice of the pore diameter of the support and the size and structure of bonded ligands. Nitrogen adsorption measurements including low-pressure data were shown to be a powerful tool to characterize structural and surface properties of unmodified and surface-modified novel porous materials.

1. Introduction

The discovery of ordered mesoporous materials (OMMs), i.e., the M41S family of silicas and aluminosilicas,[1,2] opened up a wide range of opportunities in fundamental research and application in various fields of technology.[1−9] OMMs with various pore sizes,[1−16] structures of pore networks,[1−9] and compositions[3,6−9,17−21] have been developed. Moreover, surface properties of OMMs were shown to be readily modified by deposition of metal and oxide particles,[6,7,9] ion exchange,[6,9,22] grafting of inorganic species,[6,7,9] and chemical bonding of organic ligands.[1,23−39]

Recently, the synthesis and application of siliceous ordered mesoporous materials with covalently bonded organic species, either via surface modification[1,23−39] or direct synthesis,[17−21] have attracted much attention. There are many reasons to expect a rapid growth of research in this direction. First of all, covalent bonding of organic species, especially organosilanes, onto silica surface has been extensively studied in the past.[40,41] A wide variety of materials with tailored surface properties have been synthesized and found applications in many areas of science and technology, e.g., in analytical and preparative chromatographic separations as well as in solid-phase extraction.[40] In addition, the number of possible structures of organic ligands, which can be bonded to the silica surface, appears to be unlimited, allowing for custom-tailoring of surface properties for desired applications. Finally, the use of OMMs as supports for bonded phases provides an additional opportunity for fine-tuning of both pore structure (pore size, shape, and connectivity) and surface properties of inorganic−organic composite materials.

Studies reported to date showed that silica-based OMMs with covalently bonded organic ligands can be used as catalysts with desired properties[20,36−39] or as highly efficient adsorbents for removal of heavy metal ions from water.[28−30] Moreover, it was shown that modification of ordered mesoporous materials via bonding organosilyl groups significantly improves their hydrothermal and mechanical stability.[25] Therefore, organic-modified OMMs promise to be highly stable materials with engineered properties, suitable for advanced applications. Modifications via chemical bonding of organic ligands, e.g., organosilanes, appear to be especially appealing due to the flexibility of choice of both organic modifiers with required size and functionality and mesoporous supports of desired structural properties (pore size, shape, and connectivity) and composition.

The development of custom-tailored materials depends not only on the feasibility of synthesis of the desired structures but also on the characterization techniques, which provide detailed, accurate, and reliable information about the structure, i.e., the specific surface area, pore size and shape, pore size distribution, surface functionality, etc. The specific surface area and pore

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* Corresponding author. E-mail Jaroniec@scorpio.kent.edu; phone (330) 672 3790; fax (330) 672 3816.

[†] Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

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diameter are crucial characteristics of ordered mesoporous materials. Gas adsorption, especially nitrogen adsorption at 77 K, is currently the best available technique for determination of these properties, because it is well-established, simple, and informative. The additional advantage of the nitrogen adsorption technique is that it provides information about surface properties of porous materials.[27,42−51] Our recent studies showed that low-pressure adsorption data are strongly influenced by the presence of organic groups on the surfaces of silica-based materials, providing an opportunity to detect[45−47] or even quantify amounts of organic species.[27] An accurate assessment of pore diameters of OMMs (usually 2−6.5 nm) on the basis of gas adsorption data is still challenging, because classical theories of adsorption and capillary condensation do not describe adequately adsorption processes in such narrow mesopores.[42,52−58] In response to the need for an accurate method of pore size estimation, simple analytical formulas have recently been developed,[52] which can be used in standard adsorption methods of the mesopore analysis, especially for siliceous materials with cylindrical pores.

The current work addresses the issues of both synthesis and characterization of organic-modified ordered mesoporous materials by presenting a detailed study of structural and surface properties of a good quality MCM-41 silica modified via chemical bonding of organosilanes with wide range of sizes and functionalities. It was shown that the pore diameter and surface characteristics of organic-modified OMMs can be systematically varied by proper selection of ligands used for the modification. Nitrogen adsorption measurements including the low-pressure region were shown to be very convenient for characterization of both structural and surface properties of modified and unmodified ordered mesoporous materials.

2. Materials and Methods

2.1. Materials. The large pore MCM-41 material was synthesized via the postsynthesis hydrothermal treatment as described elsewhere.[10,15] Silanes (trimethylchlorosilane, *n*-butyldimethylchlorosilane, *n*-octyldimethylchlorosilane, *n*-octyltriethoxysilane) were acquired from United Chemical Technologies, Inc. (Bristol, PA). 3-(Aminopropyl)triethoxysilane, hexanoyl chloride, and anhydrous pyridine (99%) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Solvents used in the synthetic procedure (toluene, hexane, acetone, acetonitrile) were purchased from Fisher (Pittsburgh, PA). Deionized water was purified in-house using an Ionpure Plus 150 (Lowell, MA) reagent water system.

Modification of the MCM-41 sample with chlorosilanes was carried out as follows. A 400 mg sample of MCM-41 was placed in a round-bottom flask, heated in an oven at 423 K for 3 h, capped with a glass stopper, and allowed to cool to ambient temperature. To the flask were added 0.04 mol of silane (trimethylchlorosilane, *n*-butyldimethylchlorosilane, or *n*-octyldimethylchlorosilane) and 0.04 mol of anhydrous pyridine, and the mixture was refluxed for 15 h. After cooling to ambient temperature, dry toluene was added to remove the excess silane and pyridine. Then, the sample was collected on a sintered glass funnel and washed with toluene, hexane, acetone, 70:30 acetonitrile−water solution, and acetone and dried in an oven at 423 K for 1 h. Elemental analysis measurements showed that no nitrogen was present in the modified materials, indicating that pyridine and pyridinium chloride were effectively removed during the washing procedure. The modification of MCM-41 with octyltriethoxysilane was carried out as described above, but the MCM-41 material was not heated prior to the reaction in order to retain a significant amount of physically adsorbed water. The samples modified with trimethylchlorosilane, *n*-butyldimethylchlorosilane, *n*- octyldimethylchlorosilane, and *n*-octyltriethoxysilane will be denoted as TMS, BDMS, ODMS, and OS-P (P stands for polymeric), respectively.

For the surface modification of MCM-41 with 3-(aminopropyl)triethoxysilane, 500 mg of MCM-41 was placed in a round-bottom flask. Then, 50 mL of dry toluene and about 0.02 mol of silane were added, and the mixture was refluxed for 18 h. After cooling to ambient temperature, the sample was washed with toluene, water, and acetonitrile and dried at 373 K for 12 h. The modified sample will be referred to as APS-P. The aminopropyl bonded phase was further modified to obtain an amide phase. A 150 mg sample of APS-P was placed in a round-bottom flask, and 10 mL of dry toluene was added. Subsequently, a solution of 0.008 mol of hexanoyl chloride and 0.008 mol of pyridine in 20 mL toluene was introduced, and the mixture was refluxed for 12 h. The obtained material was washed with toluene, acetonitrile, 1:1 (v/v) acetonitrile−water mixture, and acetonitrile and dried in an oven at 373 K for 15 h. The hexanoyl-3-aminopropyl bonded polymeric phase will be denoted as HAPS-P.

2.2. Measurements. Elemental analysis measurements were performed using a LECO CHNS-932 elemental analyzer (St. Joseph, MI). Thermogravimetric analysis was carried out in nitrogen atmosphere on a high-resolution TGA 2950 thermogravimetric analyzer from TA Instruments, Inc. (New Castle, DE). Nitrogen adsorption isotherms at 77 K were measured using a Micromeritics ASAP 2010 volumetric adsorption analyzer (Norcross, GA). Prior to the adsorption measurements, samples were outgassed for 2 h at 473 K (unmodified MCM-41) or 413 K (modified samples).

2.3. Calculation Methods. Specific surface areas of the materials under study were calculated using the standard BET method[53,59−61] on the basis of adsorption data in the range of relative pressures from 0.04 to 0.2. The total pore volume was estimated from the amount adsorbed at p/p_0 of about 0.99.[53] The primary mesopore volume and the external surface area were calculated using the high-resolution α_s plot method[48,53,62] from the data in the α_s range from 1.8 to 2.4, as described in detail elsewhere.[15,44] A macroporous silica gel LiChrospher Si-1000 (EM Separations, Gibbstown, NJ) was used as a reference adsorbent.

Pore size distributions were calculated from adsorption branches of nitrogen isotherms applying the BJH method[63] with the corrected form of the Kelvin equation for capillary condensation in cylindrical pores:[52]

$$r(p/p_0)\ [\mathrm{nm}] = 0.416[\log(p_0/p)]^{-1} + t(p/p_0) + 0.3 \qquad (1)$$

where r is the pore radius, p is the equilibrium vapor pressure, p_0 is the saturation vapor pressure, and $t(p/p_0)$ is the statistical film thickness curve (t-curve) as a function of the relative pressure. The t-curve used in the current study was based on the nitrogen adsorption isotherm for a macroporous silica gel and has an accurate analytical representation in the relative pressure range from ca. 0.1 to 0.95:[52]

$$t(p/p_0)\ [\mathrm{nm}] = 0.1\left[\frac{60.65}{0.03071 - \log(p/p_0)}\right]^{0.3968} \qquad (2)$$

Equation 2 is particularly suitable for siliceous adsorbents and is expected to be somewhat less accurate for materials of different surface properties.

Pore diameters for the samples modified with alkyldimethylsilyl groups were also estimated on the basis of the primary mesopore volumes and carbon contents, according to the following formula:

$$w_{\mathrm{mod}} = w_{\mathrm{BJH,MCM-41}} \times \left(\frac{V_{\mathrm{p,mod}}}{V_{\mathrm{p,MCM-41}}[1 - \%\mathrm{C}(M - 1.008)/(12.011 n_{\mathrm{c}})]}\right)^{1/2} \quad (3)$$

where w_{mod} stands for the pore diameter of the modified material and $w_{\mathrm{BJH,MCM-41}}$ is the pore size of the MCM-41 support obtained from the BJH method as described above. $V_{\mathrm{p,\ mod}}$ and $V_{\mathrm{p,\ MCM-41}}$ are primary mesopore volumes for the modified and unmodified MCM-41, respectively. M is the molecular mass of the bonded ligand (i.e., $-\mathrm{Si(CH_3)_2R}$), n_{c} is the number of carbon atoms in the ligand, and %C is the carbon content in the sample. Equation 3 is based on the assumption that the lowering of the primary mesopore volume observed after the modification can be attributed to the decrease in the pore diameter and the increase in the mass of the sample as a result of the replacement of hydrogen atoms on silanol surface groups by the organosilane ligands. It should be noted that eq 3 is difficult to apply for polymeric stationary phases (e.g., APS-P, HAPS-P, and OS-P), since there is some uncertainty about their exact structure. The previous work[46] showed that side ethoxy groups attached to the silicon atoms of the bonded ligands are expected to be completely hydrolyzed during the synthesis or washing. However, the side silanols formed may condense to some extent with other silanols, leading to formation of cross-linked polymeric bonded phase of complex structure.

Adsorption energy distributions (AEDs)[49] were obtained using the INTEG program[50] based on the regularization method. The local adsorption behavior was represented by the Fowler–Guggenheim adsorption isotherm, and the random distribution of adsorption sites was assumed. The details of calculations and the parameters used were described elsewhere.[46,47,50] The AEDs are normalized, and therefore they reflect relative populations of adsorption sites per unit area of the material, rather than their absolute amount per unit mass. Exact values of adsorption energies and details of shape of the AEDs obtained using the INTEG program are dependent to some extent on the local adsorption model chosen and on the parameters used in calculations.[42,45,50] However, these relatively small differences are not expected to significantly influence the comparative analysis of AEDs calculated in the same way for a series of samples, which is the case in the current study.

The surface coverages of organic ligands were estimated on the basis of the BET specific surface area of the MCM-41 support and the carbon contents from elemental analysis, as described elsewhere.[64] For polymeric phases (i.e., OS-P, APS-P, and HAPS-P), it was assumed that (i) all ethoxy groups of the chemically bonded silanes were hydrolyzed during the washing procedure, but the silanols formed did not condense to form siloxane bridges between adjacent organosilane groups or with the silica surface, and (ii) all bonded silanes are attached to the surface (rather than to other organosilane groups) via a single siloxane bridge.

3. Results and Discussion

Structural properties of the large pore MCM-41 used as a support for the synthesis of the bonded organosilane phases were described in more detail elsewhere,[65] and it was demonstrated that the sample exhibits a significant degree of ordering (four peaks on XRD spectra) and exceptionally high hydrothermal stability. Listed in Table 1 are contents of carbon in the modified samples and surface coverages of organosilanes. The attained coverages were similar for all samples (2.5–3.0 mmol/m^2), but in the case of materials with alkyldimethylsilyl ligands, a slight decrease in the surface coverage with the increase in the length of alkyl groups was observed. The elemental analysis results indicated that the conversion of amine groups to amides was not complete (approximately 80% of amine groups reacted), and therefore the bonded amide phase (HAPS-P) contained some residual 3-aminopropyl ligands (Table 1).

TABLE 1: Structural Properties of the Unmodified Large Pore MCM-41 and the Samples Modified by Chemical Bonding of Organosilanes[a]

sample	S_{BET} (m^2/g)	V_{p} (cm^3/g)	V_{t} (cm^3/g)	% C	SC (μmol/m^2)	w_{BJH} (nm)
MCM-41	930	0.98	1.00			5.0
TMS	660	0.65	0.67	8.38	2.97	4.5
BDMS	550	0.53	0.54	13.8	2.65	4.3
ODMS	440	0.38	0.39	20.1	2.51	3.8
APS-P	560	0.51	0.53	6.91	2.7	4.4
HAPS-P	360	0.29	0.29	15.4	2.1[b]	3.8
OS-P	540	0.46	0.48	17.0	2.8	4.0

[a] S_{BET} = BET specific surface area; V_{p} = primary mesopore volume; V_{t} = total pore volume; % C = weight percent of carbon in the samples; SC = surface coverage of chemically bonded ligands; w_{BJH} = primary mesopore size. [b] In addition to the hexanoyl-3-aminopropyl ligands, the HAPS-P sample contains 0.6 mmol/m^2 of unreacted 3-aminopropyl groups.

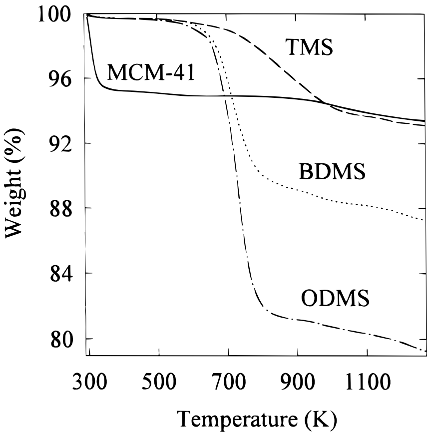

Figure 1. Weight loss curves for the unmodified MCM-41 and for the samples with bonded trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl groups.

Thermogravimetric weight loss curves for the materials under study are shown in Figures 1 and 2. It can be seen that the unmodified MCM-41 exhibited a major weight loss at temperatures up to ca. 373 K, which can be attributed to the release of physically adsorbed water[46,66] and therefore indicates a relatively hydrophilic character of its surface. At higher temperatures, the TGA curve was very flat, especially up to ca. 873 K, showing that there is no appreciable condensation of silanol groups on the surface of the material.[46,66] The weight loss profile of the MCM-41 material was significantly altered as a result of the modification. In the case of samples with alkyldimethylsilyl bonded ligands (see Figure 1), the weight loss up to 373 K was very small, revealing the hydrophobic character of the materials, which can be expected because of the appreciable surface coverage of hydrophobic alkyl groups. Hydrophobicity of ordered mesoporous materials with bonded trimethylsilyl groups has already been reported by others.[1,25] At higher temperatures, the TGA curves were initially flat and then exhibited a rapid decline in the temperature range from

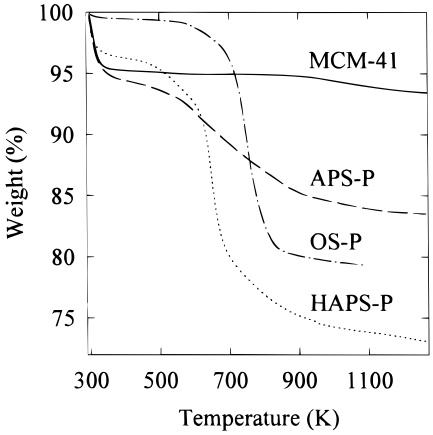

Figure 2. Weight loss curves for the unmodified MCM-41 material and for the aminopropyl, hexanoyl-3-aminopropyl, and octyl polymeric bonded phases.

ca. 650 to 1000 K (the exact temperature range was dependent on the nature of bonded ligands), followed by a more gradual weight loss. The prominent steps on the TGA curves can be attributed to the decomposition of bonded organosilane moieties,[45,46] and their height is roughly proportional to the carbon contents in the samples. As can be seen in Figure 2, the weight loss profile for aminopropyl bonded phase exhibited a sharp decrease at $T < 373$ K, showing the presence of a significant amount of physically adsorbed water. Due to a relatively small size of aminopropyl ligands, water molecules are expected to interact not only with amine groups but also with side silanols of bonded organosilanes and with silica silanols, which may account for a relatively strong affinity of APS-P to water. The comparison of TGA data for APS-P and HAPS-P shows that the initial weight loss (below 373 K) decreased, and the height of the step associated with the decomposition of organic groups increased as a result of amidization of amine groups. The decrease in the amount of physically adsorbed water can be attributed to the introduction of the hydrophobic hexanoyl groups to the structure of bonded silanes. The polymeric OS-P octyl bonded phase exhibited a weight loss profile similar to those of alkyldimethylsilylated materials, showing that the side silanols of the bonded ligands and the surface silanols are effectively screened by long aliphatic chains and inaccessible to water molecules. It needs to be noted that for polymeric bonded phases (APS-P, HAPS-P, and OS-P), the weight loss above ca. 473 K can be attributed not only to the decomposition of the bonded ligands but also to the condensation of the ligand's side silanols with one another or with surface silanols.[46]

Nitrogen adsorption isotherms for the materials under study are shown in Figures 3 and 4. The BET specific surface areas, primary mesopore volumes, and total pore volumes are listed in Table 1. The unmodified MCM-41 exhibited a sharp step of capillary condensation in primary mesopores at the relative pressure of ca. 0.5, indicating a narrow pore size distribution of the material. The adsorption isotherm was very flat in the high-pressure region (above p/p_0 of about 0.6), providing a direct evidence for low external surface area and insignificant secondary mesoporosity. It can be seen that after modification the surface area and pore volume decreased significantly. The extent of such a decrease was dependent on the size of bonded groups, which is expected since the surface coverages of ligands were comparable (see Table 1). The overall shape of adsorption isotherms remained unchanged, and the pronounced steps of capillary condensation in primary mesopores were evident, indicating that ordering of the MCM-41 support was not affected by the modification. However, the position of the capillary condensation steps gradually shifted to lower pressure values with the increase in size of the bonded ligands. This shift was accompanied by a gradual disappearance of the hysteresis loop. For the unmodified sample, a pronounced hysteresis loop was observed, but in comparison to the adsorption branch, the desorption branch was somewhat steeper, especially near its lower closure point, due to the proximity of the region of transition between the irreversible and reversible adsorption behavior (relative pressure of ca. 0.4).[52,53] In the case of TMS, BDMS, and APS-P, there were triangular hysteresis loops with very steep desorption branches, and for HAPS-P, the adsorption−desorption process was almost fully reversible with a hardly visible hysteresis loop at a relative pressure of ca. 0.4.

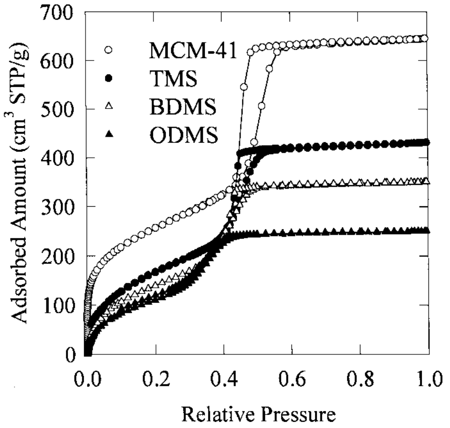

Figure 3. Nitrogen adsorption isotherms for the unmodified MCM-41 and for the samples with bonded trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl groups.

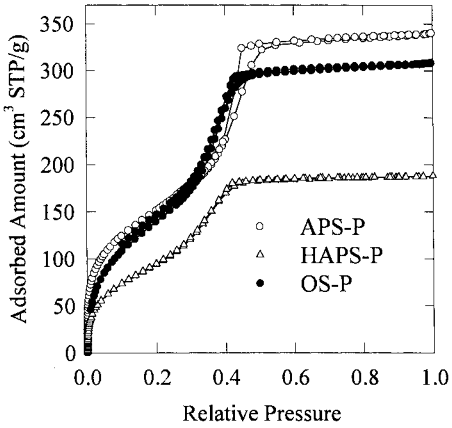

Figure 4. Nitrogen adsorption isotherms for the aminopropyl, hexanoyl-3-aminopropyl, and octyl polymeric bonded phases.

MCM-41-based octyl-bonded stationary phases (ODMS and OS-P) showed an interesting behavior, as their nitrogen adsorption isotherms were not reversible at relative pressures below 0.4, giving rise to a low-pressure hysteresis (see Figures 3 and 4). Typically, such hysteresis loops can be attributed to the presence of constrictions in porous structures or to swelling of the adsorbent during the adsorption process.[53] In the present case, the influence of constrictions can probably be precluded, since there is no low-pressure hysteresis for HAPS-P, which has the largest ligands among the modified samples considered. As far as the swelling is concerned, it is not likely that it would affect only the octyl-modified materials and would not take place for the other bonded phases. However, the low-pressure hysteresis for materials with octyl groups may result from very weak interactions between nitrogen and long aliphatic chains.

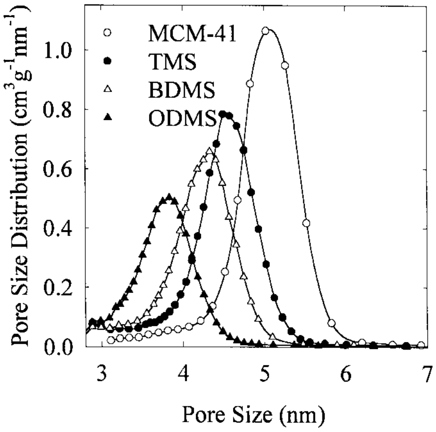

Figure 5. Pore size distributions for the unmodified MCM-41 and for the samples with bonded trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl groups.

It was reported that hydrocarbons, such as cyclohexane and *n*-hexane, adsorbed on a graphite surface exhibited immiscibility or low miscibility with nitrogen at 77 K.[67] In the case of preadsorbed cyclohexane, the increase in pressure of nitrogen led to the displacement of preadsorbed hydrocarbon from a part of the surface, rather than to the formation of a mixed phase. Our previous studies and current results described below indicated that interactions of nitrogen adsorbate with surfaces of octyl-modified silicas are very weak in comparison to those observed for unmodified silicas and many silica-based bonded or coated phases.[45−47] Therefore, it can be speculated that the formation of nitrogen film on the surface may cause changes in the configuration of octyl-bonded groups in order to diminish unfavorable interactions. Alternatively, during the adsorption−desorption process, some nitrogen molecules may cross the layer of bonded octyl groups and reach high-energy adsorption sites of the silica surface (or possibly side silanols and/or cross-linking siloxane groups in the case of the bonded polymeric phase OS-P). These higher energy sites might also become accessible as a result of the aforementioned hypothetical change in configuration of octyl groups. Further studies are needed to obtain more insight into the appearance of the low-pressure hysteresis for materials with bonded octyl groups.

Pore size distributions calculated for the unmodified MCM-41 and the modified materials using the BJH method with the corrected form of the Kelvin equation (eq 1) are shown in Figures 5 and 6, and the resulting pore sizes are listed in Table 1. Shown in Figure 7 are pore diameters for the MCM-41 materials bonded with alkyldimethylsilyl groups as a function of the number of carbon atoms in the alkyl chain. The results from the BJH method (with eq 1) and the calculations based on eq 3 are very similar (differences below 0.15 nm), showing the consistency of procedures used for pore size analysis. Moreover, the data obtained by means of eq 3 are systematically smaller, which can be explained by weaker interactions of nitrogen with surfaces of modified materials than with the surface of the unmodified MCM-41 silica. Consequently, the statistical film thickness provided by eq 2 may be slightly overestimated, which would possibly lead to a small overestimation of pore sizes for the modified materials, when calculations are based on eqs 1 and 2.

As can be seen in Figures 5−7, a systematic decrease in the pore diameter with the increase in size of bonded ligands was observed, clearly demonstrating that the surface modification indeed took place inside the primary mesopores of the MCM-41 support. The attained pore diameters covered the range from 5.0 down to 3.8 nm (see Figure 7 and Table 1), showing that the pore size can be tailored in a wide range using the chemical bonding procedures applied in the current work. For alkyl groups, the thickness of the layer of the bonded ligands can be qualitatively estimated from data shown in Figure 7, but it must be kept in mind that its actual value will be dependent on the surface coverage of bonded groups and on the pore size of the support, due to the effects of the surface curvature on the arrangement of alkyl chains in the bonded phase. It is thus expected that the introduction of different ligands of similar size should cause a comparable decrease in the pore diameter, provided surface coverages of bonded groups are comparable. An examination of the pore size data for two types of octyl bonded phases (ODMS and OS-P) showed that this was actually the case. It can be concluded that when reproducible surface coverages of bonded groups can be attained, it is easy to predict the resulting pore size of the modified material knowing the pore size of the inorganic support and the effective thickness of the bonded layer formed during modification with given ligands. This provides a simple methodology to synthesize materials with custom-tailored pore dimensions,[30] since the pore size of ordered mesoporous materials, especially MCM-41 and similarly structured solids, can be readily varied in the range from 2 to 30 nm.[1−16]

The analysis of low-pressure nitrogen adsorption data allowed us to study changes in surface properties of the MCM-41 materials caused by the chemical modification. To effectively

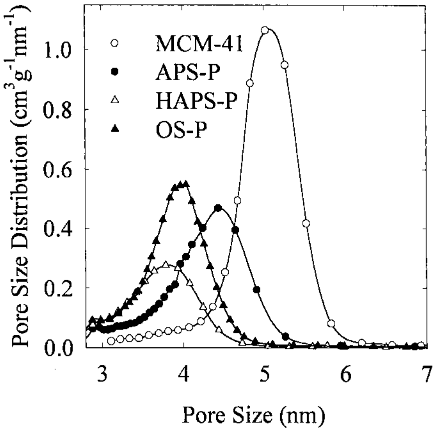

Figure 6. Pore size distributions for the unmodified MCM-41 and for the aminopropyl, hexanoyl-3-aminopropyl, and octyl polymeric bonded phases.

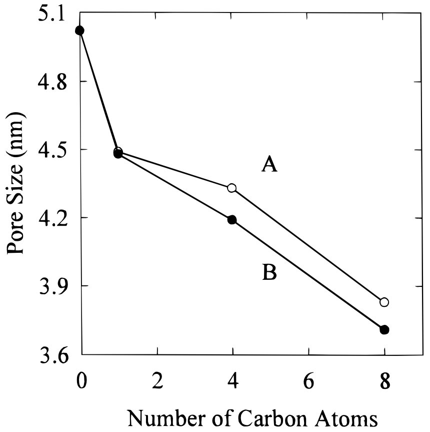

Figure 7. Relation between the pore size of alkyldimethylsilyl-modified MCM-41 materials and the number of carbon atoms in *n*-alkyl chains. The pore size was assessed using the BJH method with eq 1 (A) and the pore volume data through eq 3 (B).

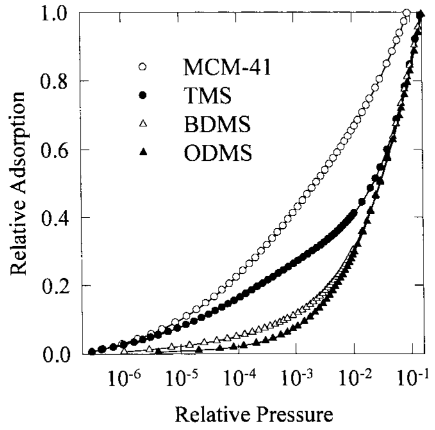

Figure 8. Low-pressure parts of relative adsorption curves for the unmodified MCM-41 and for the samples with bonded trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl groups.

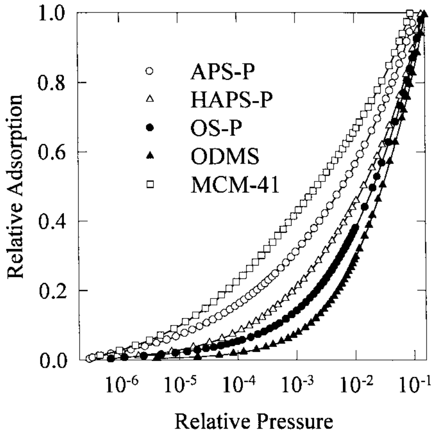

Figure 9. Low-pressure parts of relative adsorption curves for the unmodified MCM-41, the octyldimethylsilylated MCM-41, and the aminopropyl, hexanoyl-3-aminopropyl, and octyl polymeric bonded phases.

compare low-pressure data, adsorbed amounts for the samples were normalized, dividing them by the monolayer capacities calculated according to the BET method. The obtained relative adsorption curves are shown in Figures 8 and 9. One can notice that the low-pressure adsorption is dramatically reduced in the presence of organic ligands, especially in the case of large nonpolar groups.[45−47] For a series of samples with bonded alkyldimethylsilyl groups, the initial parts of the relative adsorption curves gradually decreased as the length of the alkyl chain increased (Figure 8). Despite its highest surface coverage among the alkyldimethylsilylated materials, the TMS-modified sample still exhibits appreciable low-pressure adsorption. It was reported previously that for trimethylsilylated samples the surface silanols were not fully screened by relatively small TMS ligands and hence accessible for adsorbate molecules (i.e., water).[68] Therefore, one can expect that in the case of the TMS sample residual surface silanols and siloxane bridges are not fully screened by TMS ligands and therefore can interact with nitrogen molecules. It is interesting to note that the surface of the TMS-modified material appeared to have low affinity for water, similarly to BDMS and ODMS, as shown from the TGA data (Figure 1). However, the latter materials exhibited much lower nitrogen adsorption in the low-pressure region. This might indicate that in the case of the TMS sample nitrogen molecules were able to probe the surface more effectively than water molecules. Alternatively, the modified surface may have a small amount of silanols capable of interacting strongly with water molecules (e.g., vicinal silanols[69]), and water molecules are only weakly attracted to other silanols and the siloxane bridges. However, both silanols and siloxane bridges may exhibit relatively strong interactions with nitrogen molecules, causing adsorption of an appreciable amount of nitrogen at low pressures. The proposed interpretation is in agreement with the TGA data, since only a small weight loss is observed for the MCM-41 material at temperatures from 473 to 873 K, indicating a small population of vicinal silanols, which are likely to condense in that temperature region and form siloxane bridges by releasing water. Further studies will be required to fully explain the observed behavior of the TMS-modified materials with respect to water and nitrogen.

It can be noticed that the derivatization of the surface by long-chain alkylsilanes (i.e., with octyl groups) caused a significant decrease in the low-pressure adsorption of nitrogen. The effect is more pronounced for the monomeric octyl phase (ODMS) than for the polymeric phase (OS-P), despite similar surface coverage (Figure 9). This indicates that nitrogen molecules were able to penetrate to some extent the layer of bonded octyl groups and to interact with side silanols of the OS-P moieties or even with the silica silanols. The former interactions probably take place to a higher extent, since the low-pressure adsorption for the butyldimethylsilyl-modified material (BDMS), which has a much shorter alkyl chain, was lower than that for the OS-P phase (compare Figures 8 and 9). It can be seen that the decrease in the chain length from octyl to butyl, and consequently, a better access of nitrogen molecules to the surface, has a smaller influence than the presence of side silanols in the polymeric bonded phase. One can also notice that the introduction of relatively small aminopropyl ligands with polar amine groups caused a quite limited decrease in the low-pressure adsorption, in comparison to the alkyl-bonded phases. As expected, the derivatization of amine groups to obtain the amide-bonded phase with nonpolar hexanoyl groups resulted in a noticeable lowering of the relative adsorption curve. However, as the transformation of amine functionalities to amides is not quantitative and the bonded amide ligands contain polar groups, the low-pressure adsorption of HAPS-P is higher than that for octyl-bonded phases.

To further investigate the effects of surface modification on nitrogen adsorption properties of the materials under study, the α_s plots were calculated to compare the low-pressure adsorption on these samples with that for a macroporous reference silica gel. The amount adsorbed at low pressures on the unmodified MCM-41 was directly proportional to the amount adsorbed on the reference solid (at the same pressure values). However, comparative plots for the modified samples were bent downward,[27] which is indicative of weaker nitrogen−surface interactions than in the case of the reference silica gel.[48]

Adsorption energy distributions for the materials under study are shown in Figures 10 and 11. It can be noticed that the introduction of trimethylsilyl groups caused a decrease in the relative amount of higher energy adsorption sites and an increase in the population of low-energy sites (at ca. 5 kJ/mol). The increase in size of the alkyldimethylsilyl ligands resulted in a further depletion of high-energy sites (above ca. 12 kJ/mol) accessible to nitrogen molecules, which are absent from the AED for the ODMS octyl phase and present only in a very small quantity on the BDMS surface. It needs to be noted that the surface coverages of alkyl monomeric phases were comparable and even slightly decreased with the increase in length of the alkyl chains (Table 1). Consequently, one can expect at least the same or even a higher amount of high-energy sites

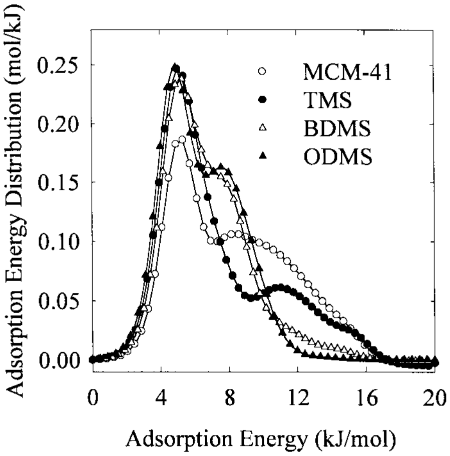

Figure 10. Adsorption energy distributions for the unmodified MCM-41 and for the samples with bonded trimethylsilyl, butyldimethylsilyl, and octyldimethylsilyl groups.

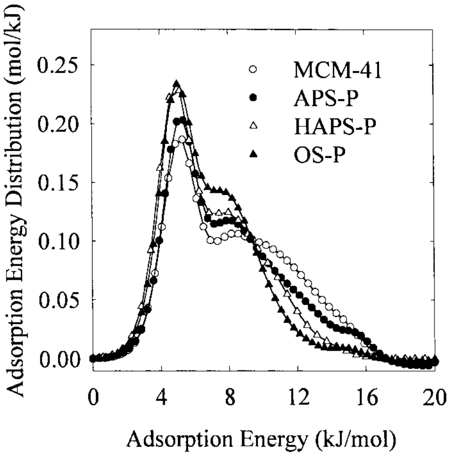

Figure 11. Adsorption energy distributions for the unmodified MCM-41 and for the aminopropyl, hexanoyl-3-aminopropyl, and octyl polymeric bonded phases.

(silanols) present on the siliceous surface of BDMS and ODMS, than is the case of the TMS sample, since the ligands were introduced via reaction with silanols, causing their partial removal to the extent proportional to the surface coverage of the bonded groups. Because of the fact that the AEDs shown in Figure 10 did not indicate the presence of high-energy sites, it can be concluded that they were effectively screened by long alkyl chains and thus not accessible for nitrogen adsorbate molecules. Therefore, in these cases, the formation of the adsorbed film appeared to take place mostly (BDMS) or almost exclusively (ODMS) on the alkyl groups.

As can be seen in Figure 11, nitrogen adsorption allowed to detect a small but noticeable population of high-energy adsorption sites on the surface of the OS-P sample, showing that the modification with monomeric octyl ligands renders the surface more homogeneous (with respect to nitrogen) than in the case of the polymeric octyl phase. The attachment of 3-aminopropyl polymeric silanes caused a relatively small change in the AED with respect to that of the unmodified MCM-41. The amount of higher energy sites decreased, whereas that of lower energy sites increased. The transformation of amine to amide moieties resulted in a further decrease in population of high adsorption energy sites at 12−16 kJ/mol.

Our previous studies showed that it is possible to attribute certain ranges of adsorption energies on AEDs to the presence of groups on the silica surface and/or in the structure of bonded or coated phases,[45−47] but it must be kept in mind that only the sites accessible to nitrogen adsorbate can effectively be probed. Consequently, adsorption measurements provide information about these accessible sites, and it is usually not possible to distinguish whether a given type of adsorption site was removed or became effectively screened as a result of the modification. Therefore, the statements about the presence or absence of certain adsorption sites should be understood accordingly.

On the basis of the discussion presented above and our previous studies,[27,45−47] one can assign certain ranges of adsorption energies to the presence of specific functional groups on the silica surface and in the structure of bonded phases. Long alkyl groups (octyl, butyl) correspond to adsorption sites with the interaction energies toward nitrogen in the range from ca. 3 to 11 kJ/mol.[45,46] The presence of polar (amine, amide) or polarizable groups (phenyl, nitrile) is reflected in the presence of adsorption sites of somewhat higher energies, up to ca. 12−13 kJ/mol.[27,46,47] The highest adsorption energies (up to 16 kJ/mol) exhibited in the AEDs result from nitrogen interactions with surface silanols or with side silanols present in the bonded polymeric phase.[46] It should be noted that the values of adsorption energy may be somewhat inaccurate due to the approximations involved in the model used to calculate AEDs.

4. Conclusions

The current study showed that chemical bonding of organosilanes onto surfaces of ordered mesoporous materials allows to obtain samples with desired pore sizes and surface functionalities. In the case when reproducible surface coverages of organic ligands can be attained, it is relatively easy to predict the pore size decrease following the modification. Consequently, a proper combination of the pore diameter of the support and the size of ligands to be bonded allows us to synthesize a porous material with fine-tuned pore size. Our study also demonstrated that the surface hydrophilic−hydrophobic character can be adjusted in a wide range by choosing suitable organosilanes. Therefore, the chemical modification of ordered mesoporous materials promises to be very useful in synthesis of tailor-made porous nanostructures for advanced applications.

The nitrogen adsorption technique was found to be a versatile and very useful tool for characterization of both porous structures and surface properties of the synthesized materials. Adsorption measurements allowed for an accurate assessment of the pore size and examination of structural changes brought about by the modification procedure. Low-pressure data were suitable for characterization of the surface functionality of the obtained inorganic−organic composite materials. These advances in the structural and surface characterization are expected to facilitate the synthesis and application of novel nanostructured materials with engineered properties.

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