Adsorption, Thermogravimetric, and NMR Studies of FSM-16 Material Functionalized with Alkylmonochlorosilanes

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Two series of alkyl-modified molecular sieves were prepared using the FSM-16 mesoporous silica. The attachment of alkyl groups to the surface, the structure of the bonded layer, and changes in the mesoporous structure of the FSM-16 material upon functionalization were studied by means of high-resolution thermogravimetry, elemental analysis, nitrogen adsorption, and ^{13}C and ^{29}Si NMR. Surface coverages of attached ligands were in the range of 0.85−2.60 mmol/g. All modified samples showed a decrease in the pore size, which was in relation to the size of attached ligands. The uniformity of pores upon modification proves that the mesoporous structure of FSM-16 is retained after modification. The attachment of ligands takes place in a solvent either with a small amount of water or anhydrous indicating a direct reaction between the chlorosilane molecule and silanol groups and/or a reaction autocatalyzed by the small amount of water present on the FSM-16 surface. Nitrogen adsorption isotherms and the adsorption energy distributions calculated from these isotherms revealed the presence of highly ordered alkyl ligands and the existence of the screening effect produced by alkyl groups as a result of weak interactions of nitrogen probe molecules with attached long alkyl chains. Thermal stability of modified samples greatly depends on the conformation of attached ligands. By using appropriate solvent and/or thermal treatment of modified samples, it was possible to achieve higher ordering of attached groups and consequently higher thermal stability of the resulting bonded phases. The studies of silicon spin−lattice relaxation times T_1 support the formation of ligand structures on the surface and show that the surface accessibility greatly decreases with increasing length of attached ligands and with refinement of the ordering of ligands on the surface. Mesoporous FSM-16 material appeared to be a good model for studying functionalization of the silica surface.

1. Introduction

Silica-based materials are commonly used in industry and widely investigated for various applications in the areas of separation, catalysis, and nanotechnology. The main advantages of these materials are high surface area, good thermal and chemical stability, and well-developed porosity. The porous structure, as a key factor of all adsorbents, plays the most important role in the majority of processes such as chromatography, catalysis, and adsorption. The main characteristics of porosity are the size of pores, pore size distribution, and their shape and uniformity. Practical utility of many adsorbents mostly depends on these characteristics.

Zeolites were the only class of silica-based materials with uniform pores of sizes not larger than 1.5 nm available until the nineties, when new types of mesoporous molecular sieves, known as MCM-41 and FSM-16, were discovered.[1−4] While MCM-41 materials were synthesized by self-assembling suitable surfactant and silica mixtures,[2,3] FSM-16, which has essentially the same properties as MCM-41, was obtained by exchanging sodium cations in layered silicates (e.g. kanemite) by cationic surfactants and their subsequent restructuring.[1,4]

It was shown in proceeding works[3,5−10] that the interior surface of uniform pores of mesoporous materials have the same type of surface hydroxyl groups as regular silicas. The IR studies of different MCM-41 materials showed the presence of several types of silanols, such as free and hydrogen-bonded silanols.[5−10] These groups can be modified by organic silanes.[3] Grafting ligands on the surface of mesopores can change their hydrophobicity and improve the stability of the resulting materials. Furthermore, the attached groups change surface properties, which can be used in variety of applications such as chromatography, extraction of heavy metal cations,[11−13] synthesize immobilized compounds or metal complexes for catalytic applications,[14−22] and improve stability of MCM-41 materials.[3,23,24] Materials modified with alkyl, phenyl, and organosulfur groups were prepared using a direct synthesis with cohydrolysis of different silanes;[19,25−28] unfortunately in some cases the resulting materials possessed more broad pore size distributions or not-well-organized pores, probably due to the specificity of interactions between alkyl chains of surfactant molecules and organic groups of silanes during synthesis.

It was shown previously[29] that the chemical modification of the silica surface is not a simple condensation reaction between alkoxy (or chloro) moieties with the elimination of alcohol (or HCl) molecules. The mechanism is more or less proved for alkoxysilanes and includes prehydrolysis of silanes. However, for samples modified by monochlorosilanes it seems to be different. In general the modification process can include several steps such as hydrolysis of the silane and condensation of surface silanols with alkylsilanols, as well as conformational rearrangements of alkyl chains, which leads to the formation of an ordered and uniformly structured monolayer. The knowledge of the surface modification mechanism is essential for the synthesis

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of stable silica-based materials with grafted ligands of reproducible coverages.

The purpose of this work was to study the process of chemical modification of FSM-16 materials that have uniform pores of very similar size and large enough to accommodate big ligands and to monitor the surface changes caused by this modification with different alkylmonochlorosilanes. By using alkylmonochlorosilanes, it was possible to study the reaction mechanism of surface silanols with these silanes and the structure of the arising surface layer without complication resulting from reaction of different numbers of surface silanols with one silane molecule and/or incomplete reaction of alkoxy groups leading to the formation of multilayer. Several issues were addressed in this work including the problem of tailoring the surface and structural properties of ordered silica materials (hydrophobicity, pore diameter) by grafting organic ligands of different structure and functionality on the surface. Also, the problem of obtaining the surface structures of desired density and geometrical structure was addressed. Changes in the properties of molecular sieves such as the amount of attached groups, the structure of the surface layer, the amount of residual silanols, the specific surface area, and thermal stability of the samples were evaluated using thermogravimetric, adsorption, and spectroscopic measurements. The observed systematic changes in the sample's physical properties were related to the structure of attached modifiers.

2. Experimental Section

Materials. Mesoporous silica-based FSM-16 material was obtained from Toyota R&D Laboratory, Aichi-gun, Japan. The trimethylchlorosilane, triethylchlorosilane, tri-*n*-propylchlorosilane, tri-*n*-butylchlorosilane, ethyldimethylchlorosilane, *n*-propyldimethylchlorosilane, *n*-butyldimethylchlorosilane, *n*-octyldimethylchlorosilane, *n*-decyldimethylchlorosilane, (3,3-dimethylbutyl)dimethylchlorosilane, and cyclohexyldimethylchlorosilane were from Petrarch System Inc. (Bristol, PA). Phenyldimethylchlorosilane and dimethyloctylchlorosilane were from Aldrich Chemical Co. (Milwaukee, WI). Hexane and acetonitrile solvents (HPLC grade, water content below 0.02%) were from Fisher Scientific (Pittsburgh, PA). Toluene (water content below 0.001%) was from Aldrich Chemical Co. (Milwaukee, WI). All materials were used without additional purification.

Synthesis of Bonded Phases. Monomeric alkyl-bonded phases were synthesized by reaction of the appropriate monochlorosilane with the FSM-16 mesoporous molecular sieve without its initial treatment. All ligands were attached from toluene. Additional modifications were performed from *n*-heptane and acetonitrile to investigate the influence of solvent on the grafting process. Typical synthesis included dispersion of 0.2 g of the FSM-16 mesoporous material in 10 mL of toluene followed by addition of an appropriate amount of monochlorosilane (5-fold excess). The mixture was kept under refluxing conditions (∼110 °C) for 20−36 h. Next, this modified mesoporous material was washed many times on the glass filter with small portions of toluene to remove an excessive amount of modifier and possible products of hydrolysis. Finally, the modified mesoporous material was dried overnight in an oven (∼95−100 °C) under vacuum. To control the thermal stability of the attached monolayer of alkylsilane and to check the quality of washing, an additional extraction was performed in the Soxhlet extractor apparatus and showed that all excessive modifier was removed by plentiful washing. Modification of the silica surface was proved by means of ^{13}C and ^{29}Si NMR spectroscopy.

The following alkylsilyl groups were attached to the surface of FSM-16 (sample codes are in parentheses): trimethyl (Me3);

triethyl (Et3); tri-*n*-propyl (Pr3); tri-*n*-butyl (Bu3); ethyldimethyl (Et); *n*-propyldimethyl (Pr); *n*-butyldimethyl (Bu); *n*-octyldimethyl (Oct); *n*-decyldimethyl (Dec); (3,3-dimethylbutyl)dimethyl (33dMB); cyclohexyldimethyl (Cyclo); phenyldimethyl (Ph).

Characterization Methods. The content of carbon and hydrogen in all samples was determined using a LECO model CHNS-932 elemental analyzer (St. Joseph, MI). For each sample three measurements were done with the relative error of less than 0.1%.

TA Instruments model TA 2950 (New Castle, DE) analyzer was used to carry out high resolution thermogravimetric analysis. All thermogravimetric measurements were done in a nitrogen atmosphere. The maximum heating rate in all cases was 5 °C/min over a temperature range from 25 to 1000 °C. The accuracy in the weight change measurements was 0.1%.

Nitrogen adsorption measurements were done using a Micromeritics model ASAP 2010 adsorption analyzer (Norcross, GA). Adsorption isotherms were measured at −196 °C over the interval of relative pressures from 10^{-6} to 0.995 using nitrogen of 99.998% purity. Before each analysis the sample was degassed for 2 h at 150 °C under vacuum of about 10^{-3} Torr in the degas port of the adsorption apparatus. Such temperature was chosen not to destroy the immobilized surface layer and at the same time to remove adsorbed gases and water.

[29]Si single pulse and ^{13}C CP-MAS NMR experiments were performed on a Bruker NMR spectrometer model Avanchi 400DMX NMR (Bruker Instrument Inc., San Jose, CA) operating at resonance frequencies of 79.49 and 100.54 MHz for [29]Si and ^{13}C, respectively. Approximately 80 mg of material was placed in a 7 mm zirconia rotor which was spun at the magic angle with the spinning frequency of 2−2.5 kHz. Measurements were performed at room temperature; air was used as the driving and bearing gas. The total number of scans in experiments was 800−4000. A high-power decoupling was used during acquisition. Chemical shifts were externally referenced to TMS (tetramethylsilane). Several signals are typically observed in the ^{29}Si NMR spectra which correspond to silicon atoms in different chemical environments, such as siloxane Q^4 [($\equiv$Si−O−)$_4$Si*], single silanol Q^3 [($\equiv$Si−O−)$_3$Si*−OH], geminal silanol Q^2 [($\equiv$Si−O−)$_2$Si*(−OH)$_2$], or silicon from attached alkylmonochlorosilane ligands, M [($\equiv$Si−O−)Si*(R)R′$_2$]. Due to a very long spin−lattice relaxation time T_1 of low abundance [29]Si nucleus[30] the relaxation times of all Si sites should be found before running a quantitative ^{29}Si MAS NMR experiment. The standard saturation recovery method was used to obtain the spin−lattice relaxation times, T_1, for different silicon sites. The relaxation delays of 120−270 s, taken as $5T_1$ for slowest relaxing site, were used.

Calculation Methods. Specific surface areas of the FSM-16 material and modified samples were calculated using the BET method.[31,32] Adsorption data in a narrow range of relative pressures ($p/p_0 = 0.025-0.09$) were used to calculate the surface area in order to avoid the overlapping with the capillary condensation step which can appear at relatively low pressures for modified samples.

Adsorption energy distributions[33] were calculated using the INTEG program[34] based on the regularization method. The Fowler−Guggenheim adsorption isotherm was used to describe the local adsorption. Random distribution of adsorption sites was assumed to model heterogeneity of the silica surface. Calculated adsorption energy distributions were normalized. The details of calculations and the parameters used are given elsewhere.[34]

The BET specific surface area from adsorption measurements as well as carbon and hydrogen contents from elemental analysis were used to estimate the concentrations of attached ligands. Their concentrations were related to 1 g of unmodified material (C_{lig}, mmol/g) or to the unit surface area (n_{lig}, groups/nm^2).

Pore size distributions were calculated from adsorption branches of nitrogen isotherms using the BJH method[35] with corrected form of the Kelvin equation for capillary condensation in cylindrical pores:[36]

$$r(p/p_0) = \frac{0.416}{\log(p/p_0)} + t(p/p_0) + 0.3$$

Here r is the pore radius, p is the equilibrium vapor pressure, p_0 is the saturation vapor pressure, $t(p/p_0)$ is the statistical film thickness curve (t-curve) as a function of the relative pressure, and an additional term in the above equation (equal to 0.3) denotes empirical correction made in the Kelvin equation.[36]

The single pulse ^{29}Si MAS NMR experiment is equally sensitive to all silicon atoms and can provide information about the ratio between siloxane (Q^4) and silanol (Q^3) groups in different samples.[37] To calculate the concentration of different groups in the sample (Q^3, Q^4, M), the NMR spectra must be deconvoluted because of overlapping signals in the spectra.

3. Results and Discussion

Characterization of FSM-16. The FSM-16 material[38,39] is a typical representative of mesoporous molecular sieves but derived from the layered silica-based material kanemite. Ordered mesoporous materials are characterized by a high surface area of 800−1100 m^2/g and very narrow pore size distribution of ordered mesopores of 3−10 nm diameter in a honeycomblike structure. Walls of cylindrical uniform pores of such mesoporous materials are amorphous, constructed from the siloxane units (Q^4) and covered from the inside by single silanol groups (Q^3) as well as siloxane units (Q^4).[5−10,40]

The amount of silanol groups on the surface of mesoporous materials can be different due to the synthetic procedure used and also depends on the method used for their estimation. The reported numbers vary from as low as 0.8 mmol/g up to 6.9 mmol/g (5 groups/nm^2) with the average amount of 2.5−3.0 groups/nm^2.[6,7,9,10,12,25,41] Molecular dynamic simulations of MCM materials showed that for typical hexagonal structures with cylindrical pores the amount of silanol groups in the structure can be between 17 and 28% of all silicon atoms,[41,42] which is very close to the experimental data. This amount is smaller than the average number of silanols found for amorphous silicas (ca. 4.9 groups/nm^2).[43]

^{29}Si MAS NMR spectra of unmodified FSM-16 mesoporous material are shown in Figure 1. The spectrum of unmodified material is similar to that for regular silica. It exhibits relatively broad lines characteristic for amorphous silica materials.[44] Signals at −99 and −109 ppm correspond to the silanol (Q^3) and siloxane (Q^4) sites, respectively.[37,44] Geminal silanols Q^2 (signal at ca. 89 ppm) are present in the amount 0.5% or less, and such contribution cannot be unambiguously extracted by deconvolution from the relatively broad signal in ^{29}Si NMR. The observed absence of a substantial amount of Q^2 sites suggests a high degree of condensation for the particular sample of FSM-16. The amount of silanols as well as the amount of siloxane groups was found to be equal to 4.0 ± 0.1 mmol/g or ca. 2.35 ± 0.06 groups/nm^2 correspondingly.

From the data of high-resolution thermogravimetric analysis, the amount of silanol groups on the surface of the unmodified
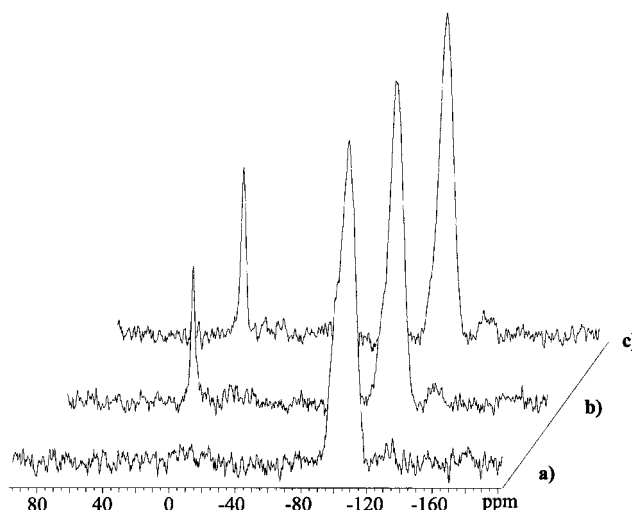

Figure 1. ^{29}Si{^{1}H} MAS spectra for the FSM-16 mesoporous materials (a) unmodified, (b) modified with octyldimethylchlorosilane, and (c) modified with trimethylchlorosilane. Chemical shifts are reported relative to the TMS.

FSM-16 material, the amount of physisorbed water, and its thermal stability can be estimated. A typical TGA curve for the unmodified sample (Figure 1S, Supporting Information) shows two representative weight losses. The first one, observed at 25−120 °C, corresponds to the removal of physically adsorbed water. The FSM-16 sample contains approximately 3.8−4.1% of physically adsorbed water (∼2.1−2.3 mmol of H$_2$O/g of the material). TGA measurements during a long period of time showed that the amount of physisorbed water in the sample greatly depends on its history and humidity of environment in which sample was stored. Physically adsorbed water can be removed from the surface of mesoporous materials under vacuum at temperature ≤ 200 °C. The weight loss in the "flat" region (200−600 °C) is 0.1% and corresponds to the removal of more strongly bonded water molecules. A continuous weight loss observed in the region of temperatures 600−1000 °C arises from the surface dehydroxylation due to structure shrinkage caused by condensation of the surface silanol groups.[6,9] The weight loss after 600 °C, which is higher than 1.6% in the case of pure mesoporous material, gives the amount of surface silanol groups larger than 1.9 mmol/g or 1.1 groups/nm^2. Such low (in comparison with results of ^{29}Si NMR) concentration of silanols that was found from TGA data can suggest a specific arrangement of silanol groups on the surface of FSM-16. For an isolated silanol which does not have neighboring silanol groups in close proximity (<5.0 Å) and in proper geometrical arrangement it is impossible to condense and form the siloxane bond without severe distortion of the structure.[44] If this assumption is correct, the surface appears to have about half of the isolated silanols and the rest arranged in such way that they are sufficiently close to each other to condense.

An important issue is the stability of MCM-41 mesoporous silica materials. Previous studies showed that MCM-type materials lost the pore ordering as well as the characteristic XRD pattern and started to show smaller surface area upon application of pressure and/or their exposure to aqueous solutions.[7,23,45−49] A test for stability was run by exposing the sample of FSM-16 to water vapor for 24 h and performing adsorption and TGA measurements periodically during a period of several months. A difference in the TGA curves is observed between untreated FSM-16 sample and samples exposed to water vapor and later dried under vacuum at 95 °C (Figure 1S). The total weight loss
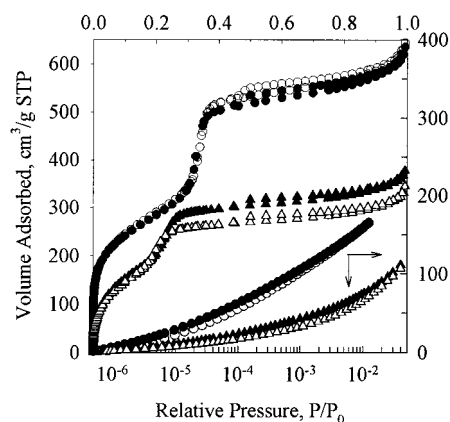
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Figure 2. Nitrogen adsorption isotherms and their low-pressure parts for the unmodified FSM-16 sample (○), FSM-16 exposed to water vapor (●), and the samples modified with phenyldimethylchlorosilane (▲) and cyclohexyldimethylchlorosilane (△).

TABLE 1: Structural Peculiarities of the Starting FSM-16 Material and the Samples Modified by Chloroalkylsilanes[a]

sample	S_{BET} (m^2/g)	C_{lig} (mmol/g)	n_{lig} (groups/nm^2)	d_{BJH} (nm)
FSM-16	1024	4.00[b]	2.35[b]	3.73
FSM-16 exposed to H$_2$O	1006			3.68
FSM-16 washed with toluene	993	0.14[c]	0.08[c]	3.67
FSM-16 washed with n-heptane	1021	0.04[c]	0.03[c]	3.71
Me	734	2.61	1.54	3.27
Et	713	2.45	1.44	3.21
Pr	685	2.32	1.36	3.13
Bu	652	2.24	1.32	3.06
Oct	568	1.90	1.12	2.81
Dec	549	1.82	1.07	2.67
Et3	753	1.87	1.10	3.10
Pr3	811	1.10	0.65	3.15
Bu3	840	0.85	0.5	3.08
3,3dMB	630	1.96	1.15	2.98
Ph	685	1.27	0.75	3.12
Cyclo	652	2.00	1.18	2.92

[a] S_{BET}, BET specific surface area; C_{lig}, surface coverage of bonded ligands; n_{lig}, number of attached groups per unit of surface; d_{BJH}, primary mesopore diameter. [b] Number of silanol groups obtained from the ^{29}Si MAS NMR data. [c] Amount of solvent from CHN data.

of the sample exposed to water vapor is twice higher than that for the untreated sample, 5.3% and 10.1%, respectively. The content of physically adsorbed water increases from 3.7% (ca. 2.2 mmol of water/g of material) up to 6.5% (~3.5 mmol of H$_2$O/g of SiO$_2$). The biggest changes in comparison to the untreated sample are in the "flat" region (200−600 °C). A new peak with maximum intensity at ca. 260 °C and an additional gradual decrease in the sample weight above 350 °C are visible. These features can reflect removal of water molecules, which are more strongly bonded to the surface, but possible release of water during condensation reaction of silanols. A potential hydrolysis of constrained siloxane bonds in mesoporous material upon exposure to H$_2$O cannot be excluded.[47−49] The weight loss in the temperature interval 600−1000 °C for the sample exposed to water vapor is identical to the unexposed sample (Figure 1S) that makes possible the assumption of only a small increase in the amount of silanol groups upon water exposure.

High- and low-pressure nitrogen adsorption isotherms for the sample exposed to water vapor and unmodified FSM-16 material are shown in Figure 2. Adsorption isotherms for exposed and untreated samples are type IV according to the IUPAC classification[50] and show a capillary condensation step at p/p_0 ~0.35 and a hysteresis loop. Changes in the BET surface area and the size of primary mesopores upon treatment are listed in the Table 1. The surface area, monolayer capacity, and calculated pore size (see results below) for unmodified sample were the same over the period of several months. On the other hand, the sample exposed to water vapor showed a small decrease in the BET surface area ca. 1.5% but the shape of adsorption isotherm and the position of the capillary condensation step still remain the same. Absence of changes in the untreated sample and very small changes in the sample exposed to water vapor can prove the stability of the FSM-16 sample with time and to environment humidity.

To check the stability of the FSM-16 material under modification conditions a series of blank syntheses was done. The blank syntheses were performed by refluxing mesoporous material in solvents (toluene or n-heptane), which were used during modification procedure, following by washing with corresponding solvent and drying the samples at 95−100 °C in the vacuum oven. Data of TGA analysis showed an increased weight loss due to solvent molecules adsorbed inside mesopores. The amount of adsorbed toluene (Table 1) was almost four times higher than heptane, which indicates stronger interactions of toluene with the silica surface of the mesoporous material studied despite evacuation of the solvent treated samples. It is

interesting to note that the total amount of water on the surface of the mesoporous silica sample remains the same, despite treatment with anhydrous solvents followed by evacuation and heating. The weight loss profile and the amount of water released upon condensation of silanols at high temperatures were unchanged for samples subjected to blank synthesis.

Adsorption measurements for samples from blank synthesis showed a slight decrease in the surface area of the sample (ca. 3%) that was refluxed in toluene and no change for the sample exposed to n-heptane. Calculations of pore size distributions showed a distinct decrease in the pore diameter (ca. 0.06 nm) for the sample treated with toluene and almost no change for the sample refluxed in n-heptane. Adsorption energy distributions calculated for the samples subjected to the blank synthesis (not shown) had no changes for the sample refluxed in n-heptane and a small increase in the amount of high energetic sites for the sample exposed to toluene. The same tendency of increasing high energetic sites was observed for the FSM-16 material upon exposure to water vapor.

Chemical Modification of FSM-16. The concentration of immobilized ligands and the surface coverage of attached groups are shown in Table 1. For all monomeric alkyl-bonded phases the immobilization of ligand on the surface of the mesoporous material by covalent linkage was shown by means of ^{13}C CP-MAS NMR spectroscopy (chemical shifts in the interval between 0 and 40 ppm).[51] Attachment of silane molecules to the surface of FSM-16 was also confirmed by means of ^{29}Si NMR (Figure 1). Spectra for modified samples have features similar to unmodified FSM-16. They indicate the presence of Q^3 silanols and Q^4 siloxane sites at ca. −99 and −108 ppm and an additional signal M at ca. 13 ppm, which corresponds to silane molecules attached to the surface in a monomeric fashion. The amount of residual silanols is proportional to the surface coverage of the grafted ligands, and their number is much greater for the samples functionalized with octyldimethylsilane than trimethylsilane (Figure 1).

Data of elemental analysis indicate a decrease in the surface coverage for both ligand series, ClSiR$_3$ and ClSiRMe$_2$, with increasing length of attached ligands. For the SiR$_3$-type ligands a decrease in the coverage density is more drastic. The increase in the size of groups is linearly proportional to a decrease in
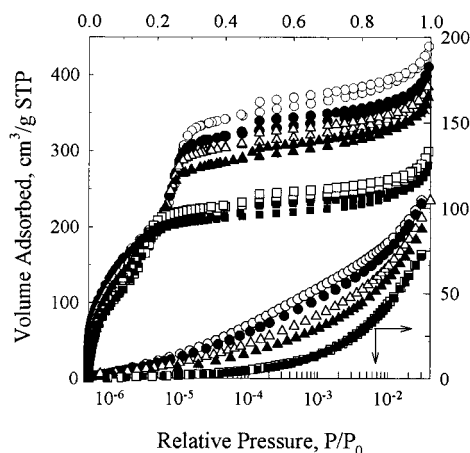
Figure 3. Nitrogen adsorption isotherms and their low-pressure parts for the FSM-16 samples modified with trimethylchlorosilane (○), ethyldimethylchlorosilane (●), propyldimethylchlorosilane (△), butyldimethylchlorosilane (▲), octyldimethylchlorosilane (□), and decyldimethylchlorosilane (■).
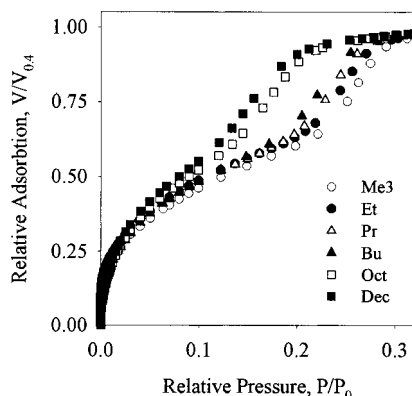

Figure 4. Normalized nitrogen adsorption isotherms showing a gradual shift in the capillary condensation step with increasing size of the ligand for the FSM-16 samples modified with trimethylchlorosilane (○), ethyldimethylchlorosilane (●), propyldimethylchlorosilane (△), butyldimethylchlorosilane (▲), octyldimethylchlorosilane (□), and decyldimethylchlorosilane (■).

the concentration of attached groups for the first homologues of both silanes, SiR_3 and $SiRMe_2$ (Figure 2S). An increase in the interaction between alkyl groups of longer carbon chains and as result more dense packing of ligands can be achieved. For ligands with R larger than propyl, the methylene groups of alkyl chains possibly start to show not only trans but also gauche configuration of ligands.[52] Several conformations could be possible for alkyl chains with terminal methyl groups either more distant from the surface (only trans configurations of methylene groups) or located close to the surface (there are gauche configurations).

Adsorption Studies of Modified FSM-16. Nitrogen adsorption isotherms for modified FSM-16 mesoporous materials are shown in Figures 2−4 and 3S; BET surface area and the size of primary mesopores are given in Table 1. The modified samples exhibit type IV adsorption isotherms[50] with the capillary condensation step gradually shifting to $p/p_0 \sim 0.20$ (Figure 4) when the length of attached ligand increases. All modified samples, despite differences in the surface coverage and the size of modifier, still exhibit a distinct condensation step on nitrogen adsorption isotherms (Figure 3).

Low-pressure adsorption data (Figures 2, 3, and 3S) show changes in the interaction of nitrogen probe molecules with the surface of the samples upon modification. By introduction of

nonpolar organic ligands on the surface of mesoporous silica adsorption is highly reduced (see Figure 2). This decrease reflects several facts related to the change in the interaction of nitrogen probe molecules with the surface, such as change in the hydrophobicity of the surface, screening of siloxane and silanol groups, and possibly structural changes in the bonded layer.

A comparison of the adsorption isotherms for Cyclo- and Ph-modified samples (Figure 2), which have ligands of similar structure and size but highly different surface coverage (2.00 and 1.27 mmol/g, correspondingly), shows high similarity of these samples. Speculations can be made about specific orientation of cyclohexane and aromatic rings on the surface. Presumably aromatic rings are tilted and lay close to the surface, whereas cyclohexane rings are oriented vertically to the surface and more densely packed. Both ligands, Cyclo and Ph, screen surface similarly as Et or Pr groups (Figure 3), but the latter have higher surface coverages, which can emphasize the importance of surface organization of attached ligands on their interaction with probe molecules and the differences in interactions between ligand molecules during modification process.

Other details are apparent from the comparison of the samples obtained with ligands that have butyl structural unit (see Figures 3 and 3S) but differ in the number of these groups (Bu and Bu3) or possesses some branches in the butyl chain (33dMB). The Bu3 phase has the lowest surface coverage and, as it was expected, the highest interaction with nitrogen. The 33dMB phase had lower coverage, lower surface area than that with Bu, and showed higher thermal stability (see TGA data). The similarity of low-pressure isotherms for the 33dMB and Bu phases indicates the same screening effect for both ligands. As can be seen, the smaller surface density of the first phase compensates by the size of additional two methyl groups in the ligand structure (located on the top of the ligand) make the screening of the surface more effective. Nonaccessibility of the surface can be governed not only by high surface concentration of the attached ligands but also by an effective packing of alkyl chains over the silica surface. As a result of a well-ordered phase, nitrogen molecules cannot penetrate the ligand layer as well as such a densely ordered layer decomposes at higher temperatures (see discussion later).

In the case of the Oct and Dec phases nitrogen adsorption isotherms exhibit the second hysteresis loop starting at $p/p_0 \sim 0.25$ and there is no closure point for high-pressure hysteresis, which turns into the low-pressure hysteresis at the inflection point at the relative pressure ca. 0.35 (Figure 3). It is possible to assume that during the adsorption process nitrogen molecules can penetrate into the layer of modifier. During the desorption process, nitrogen can be still trapped between alkyl chains of ligands and released very slowly due to weak interaction with alkyl chains or structures created by attached ligands. For trialkyl-modified samples there is an increase in the interaction of nitrogen with the surface for the samples with longer alkyl chains (Figure 3S). This indicates that nitrogen molecules penetrate the bonded layer and access the surface silanol and siloxane groups, and as mentioned above, these alkyl ligands have presumably linear structure.

For MCM-41 materials modified with monochlorooctylsilane there is a significant decrease in the interaction of nitrogen probe molecules with the silica surface in comparison to the sample modified with octyltriethoxy silane.[53] Despite the possibility of condensation between side alkoxy groups of nearest ligands and decrease in the distance between ligands, the surface silanols and the silanols formed during hydrolysis of ethoxy moieties
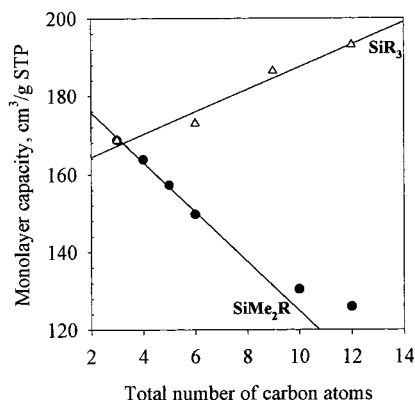
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Figure 5. Relation between the monolayer capacity of the alkyl-modified FSM-16 and the number of carbon atoms in the longest alkyl chain of the attached ligand. The FSM-16 samples were modified with $ClSiR_3$ (open triangles) and $ClSiMe_2R$ silanes (solid dots).
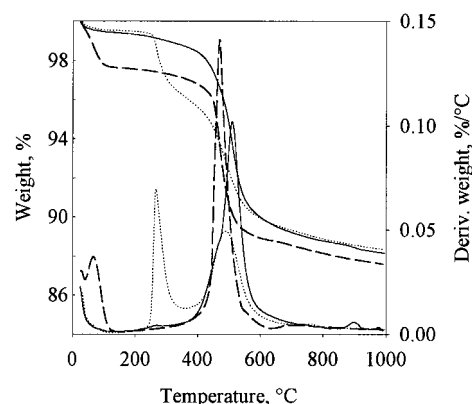

Figure 6. TG and DTG curves for the FSM-16 samples modified with butyldimethylchlorosilane of low (dotted lines) and high stability (solid lines) and the sample modified with triethylchlorosilane (dashed lines).

are still accessible. This observation and our own study of mesoporous materials modified with long alkyl groups, especially octadecyldimethylchlorosilane,[54] can be interpreted in terms of different structural organization of the surface layer. This can be further supported by possible interaction of hydrophobic alkyl moieties of the modifier with hydrophobic surface of the FSM-16[6,55] during the first step of modification. As result of the above-mentioned interactions, an island structure of the bonded layer can be formed with the areas covered by alkyl chains and the areas of exposed siloxane and silanol groups. The curvature of mesopore walls also can contribute to the formation of specific island structure.

There is a linear dependence between the monolayer capacity for modified samples and the length of alkyl chains for first homologues of alkyldimethylsilanes (Figure 5). Relatively higher surface coverages for the Oct and Dec phases were achieved than was expected. This fact indicates a tendency of linear conformation for long alkyl chains due to the specific interaction between alkyl groups. For trialkyl-modified mesoporous materials the plot of the monolayer capacity shows a small increase in the adsorption with increasing alkyl chain length due to a less dense packing of ligands on the surface (Figure 5).

Thermogravimetric Studies of Modified FSM-16. Samples modified by alkylchlorosilanes showed an increased weight loss and additional thermal effects on the TGA curves in comparison to unmodified one. For mesoporous materials modified by alkyldimethylchlorosilanes, with alkyl radicals butyl or longer, there are two distinct thermal effects on the DTG curves. One of them appears at 270 °C, and the other one, at 510 °C. The intensity of these effects depends on the treatment of samples, solvent used for synthesis, and aging time of the sample. For a given sample the highest amount of attached groups, corresponding to the first effect, is observed for the "as prepared" sample. The weight loss at 270 °C gradually decreases upon increasing storage time or/and treatment at elevated temperature ~180 °C. At the same time the weight loss at 510 °C increases (the corresponding peak starts to be very sharp), and this effect is only one that is present for the sample with "high" stability (Figure 6). Such changes on the DTG curves and the absence of changes in the total weight loss (from room temperature up to 1000 °C) on the TGA curves can suggest that some conformational changes of alkyl chains attached to the surface occur. If the modification process involves the formation of an intermediate complex of the ligand with the surface, one should observe a change in the total weight loss between "as prepared" and treated samples ~1.0−3.0% at the concentration of attached

groups 1.0−2.6 mmol/g. This change should correspond to the released hydrochloric acid or water upon condensation of surface silanol groups associated with silane or prehydrolyzed silane molecules, correspondingly.

The presence of only one sharp peak at ca. 510 °C on the DTG curve and the absence of decomposition at 270 °C for silanes with short alkyl chains (methyl, ethyl, and propyl phases) also support interpretation of this transition as conformational. Studies of thermal decomposition of ligands with "predefined" configuration (Cyclo and Ph) or a ligand with sterically hindered alkyl chains (33dMB) showed the presence of only stable ligand phases. In the case of the sample modified by trialkylsilane, for example triethylsilane, there is a thermal effect (Figure 6) with maximum at 510 °C on the TGA curve that corresponds to the decomposition of attached ligand. The temperature of the maximum decomposition rate does not depend on the thermal treatment of the sample that was shown by additional studies. The absence of possible conformational changes for these ligands as well as facts mentioned above unambiguously proves that changes upon aging with time and/or at elevated temperatures are conformational. Such aging leads to more ordered ligand coverage and results in much higher thermal stability.

Comparative studies of the solvent influence on the modification reaction were done for the octyl phase. For the three studied solvents, toluene, acetonitrile, and *n*-heptane, the highest coverage was achieved for heptane as a solvent, 1.90, 2.11, and 2.28 mmol/g (1.12, 1.24, and 1.34 groups/nm²), respectively. The TGA analysis of the freshly prepared and dried at 95 °C under vacuum samples showed a distinct difference in the thermal stability between samples prepared using the above-mentioned solvents (Figure 4S). A significant difference in the thermal stability and some difference in the coverage for the sample prepared from *n*-heptane can suggest altered conformation of octyl ligands due to specific interactions between alkyl chains of the ligand and heptane molecules during synthesis. After thermal treatment, other two samples, prepared from acetonitrile or toluene, can be switched to a more stable conformation.

The samples modified using toluene (Table 1), acetonitrile, and *n*-heptane exhibit different surface areas (S_{BET} for the samples modified from *n*-heptane and acetonitrile were 516 and 530 m²/g, correspondingly). The phases synthesized from acetonitrile and *n*-heptane show very similar low-pressure adsorption. Low-pressure adsorption behavior as well as much higher thermal stability (see results above) of the octyl phase *as synthesized* from *n*-heptane may indicate some differences in the structure of these bonded phases. It can be summarized
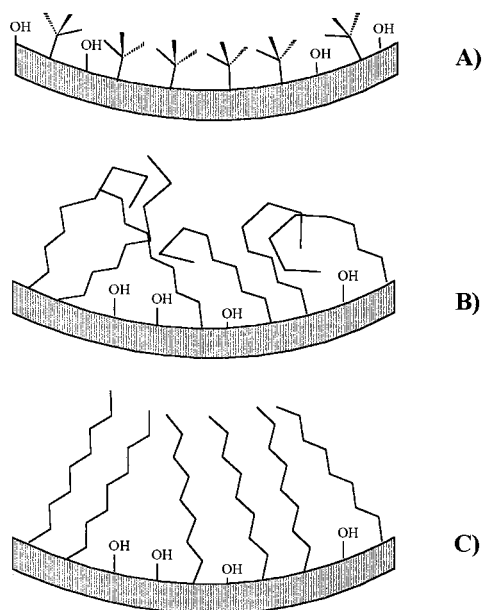
Figure 7. Schematic representation of functionalization of the internal surface of the FSM-16 mesoporous material with alkylchlorosilanes (only part of the mesoporous channel system shown): FSM-16 functionalized with $ClSiMe_2R$ silane of short alkyl chains (a) as well as long alkyl chains (octyl- or decyldimethylchlorosilane) disordered and less thermally stable (b) and ordered and thermally stable (c).

Figure 8. Adsorption energy distributions for the unmodified FSM-16 (○) and the samples functionalized with trimethylchlorosilane (●), ethyldimethylchlorosilane (△), propyldimethylchlorosilane (▲), butyldimethylchlorosilane (□), octyldimethylchlorosilane (■), and decyldimethylchlorosilane (◇).

that by changing the reaction solvent one can adjust conformation of attached groups.

An identical conclusion about correlation of the decomposition temperature of grafted ligands with conformational changes can be drawn from the data of ^{29}Si NMR spectroscopic studies. If only a gradual modification occurs and the transition observed on the DTG curves reflects further attachment of prehydrolyzed ligands to the surface, suitable changes in the ratio of the Q^3 and Q^4 sites should be observed by NMR. Also, a hypothetical complex between ligand or prehydrolyzed silane interacting weakly with the surface (less strongly than chemical bond) should be subsequently destroyed or removed upon washing with solvent, extraction in a Soxhlet apparatus, or degassing at elevated temperatures and low pressure (180 °C, 10^{-3} Torr). However, neither the unchanged Q^3:Q^4 ratio nor unsuccessful washing support the former explanation. An additional argument appears from the observed switching between "high stability" and "low stability" state for the same sample upon spinning.

On the basis of the ^{29}Si NMR and thermogravimetric studies, the following mechanism of grafting alkylmonochlorosilanes on the surface of the FSM-16 material can be proposed. Probably, the first step of modification with chloroalkylsilanes is a direct interaction of silane molecule with the surface silanol. At the same time the hydrophobic part of silane (especially one with a long alkyl chain) can interact with the hydrophobic surface of FSM-16.[9,55] It is reasonable to assume that upon formation the surface bond the attached ligand of long length shows a bent conformation. For such structures the surface layer is less uniform, can possesses open parts of the surface, and shows "low" stability. After thermal treatment the surface layer starts to be more uniform due to the straightening out of alkyl ligands oriented orthogonal to the surface and shows "high" stability (Figure 7). Also, as it was shown that by studying the solvent effect on the functionalization, the influence of intermolecular interactions between ligand molecules and solvent during modification process cannot be eliminated.
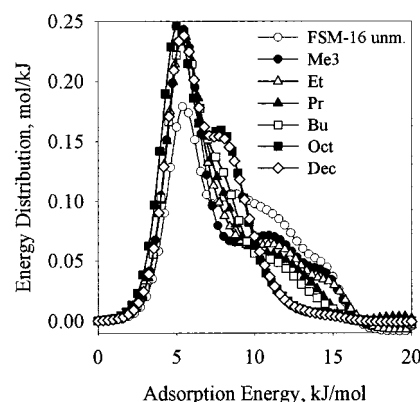
Adsorption Energy Distributions and Pore Size Analysis. Adsorption energy distributions for the samples modified with alkyldimethylsilanes are shown in Figure 8. Even reaction with the small trimethylchlorosilane led to the removal of high-energy sites (ca. 12 kJ/mol). The introduction of larger alkyl chains, especially Oct and Dec, results in the complete removal of such sites. Taking into account that the concentration of ligands with longer alkyl groups decreases (Table 1), it is reasonable to assume that two competitive processes of *removal* free silanols can occur: a "direct removal" by reaction with chlorosilanes and an "indirect removal" by coating and screening with longer and bulky alkyl chains of attached ligands. This "indirect removal", as can be seen, may not completely eliminate the possibility of penetration of probe molecules to the surface groups. The process of "indirect removal" seems to be dominating in the case of Oct and Dec phases, but this process is also occurring even for propyl and butyl phases. As result of the surface screening, one can observe an increase in the amount of low-energy sites (ca. 6 kJ/mol). For attached ligands with C_8 alkyl chains and longer there is also a contribution from the sites with energy ca. 9 kJ/mol that can be attributed to the interaction of nitrogen molecules with alkyl chains. It can be speculated that this peak in the adsorption energy distribution spectra corresponds to the interaction of nitrogen molecules penetrating into the layer of alkyl chains or into the void space traps between ligands.

Adsorption energy distributions for trialkyl-modified samples (Figure 5S) show an insignificant decrease in the interactions related to the high-energy sites at ca. 12 and ca. 15 kJ/mol. This observation, as well as the fact of a noticeable increase in the interactions related to sites with energies ca. 15 kJ/mol, which is observed for longer trialkyl chains, and a decrease in the ligand's concentration on the surface, can support conclusions about accessibility of the surface silanols and siloxane bridges in such samples for nitrogen probe molecules. As it was mentioned above, steric factors play an important role in the attachment of bulky trialkyl ligands to the surface and led to the materials with a sparsely packed ligand layer. The importance of steric factors on the bonding of alkylsilanes can be seen by comparing adsorption energy distributions for the samples modified with alkyl ligands of similar length but different structures (see Figures 8 and 5S). Upon change of the bulky tributyl ligand to the compact linear butyldimethyl one there is a complete removal of highly energetical sites. Even addition of small methyl groups into the main butyl chain of the 33dMB ligand makes interaction between long alkyl groups
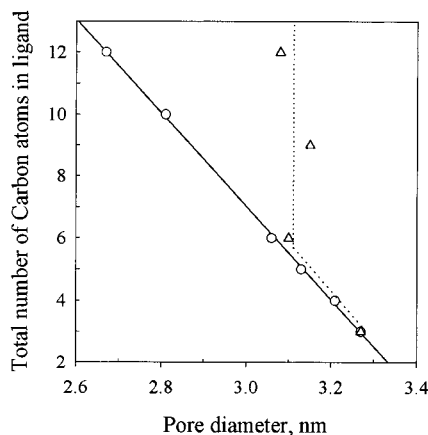
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Figure 9. Relation between the pore width for the FSM-16 sample functionalized with ClSiMe$_2$R (solid line and empty dots) and ClSiR$_3$ (dotted line with empty triangles) and the number of carbon atoms in the longest alkyl chain of the attached ligand.

not so effective and leads to appearance of a small amount of high-energy sites accessible to nitrogen molecules. However, it should be noted that, because of the screening effect of alkyl ligands, the disappearance of peak on the energy spectra does not always mean the removal of the corresponding groups or sites.[53]

A graphical representation of systematic changes in the pore diameter with increasing size of attached ligands is shown in Figure 9. For "linear" dimethylalkyl ligands an increase in the length of the main ligand's chain led to a gradual decrease in the pore diameter. For the "branched" trialkyl ligands the graph is more complex, and as was mentioned before, its curvature can be due to an increase in the amount of gauche conformation of attached alkyl chains. In addition, the factor of the decreasing surface coverage with increasing size of grafted silanes should be taken into account. In such cases, structures with almost constant (at least for studied tributyl-, tripropyl-, and triethyl-chlorosilanes) pore width ca. 3.1 nm were obtained.

^{29}Si NMR Studies of Longitudinal Relaxation Times. Valuable information about structure of the ligand layer can be obtained from analysis of longitudinal relaxation time T_1 for different silicon species on the surface. ^{29}Si nuclei have several pathways for the spin−lattice relaxation which arise from the dipole−dipole interaction with the nearby mobile protons of water molecules present in the sample, interaction with the unpaired electrons of present paramagnetic metal ions (such as iron), or interaction with paramagnetic molecular oxygen. Previous studies of zeolites with different Si/Al ratio showed that the longitudinal relaxation time T_1 does not depend on the content of aluminum in the structure, but there is a strong dependence on the amount of oxygen present in the atmosphere surrounding the sample,[56,57] hydration of the sample, or introduction of different organic molecules (solvent).[56,58] It is difficult to isolate the specific influence coming from the oxygen or solvent on the relaxation process in different samples of silica materials, but the effect of present oxygen is larger than the hydration effect.[57]

It is apparent that upon modification of the FSM-16 meso-porous material by organosilane there is a substantial decrease in the access of "relaxation sources" to the silicon nuclei and for all samples the longer relaxation times are observed for Q^4 and Q^3 sites (Figure 10). The longitudinal relaxation time for silicon atom with monodentately attached ligand (M) is typically 1.3−3.2 times shorter than for Q^4 and Q^3 silicons. T_1 values for M-type silicon increase up to 26−28 s with decreasing
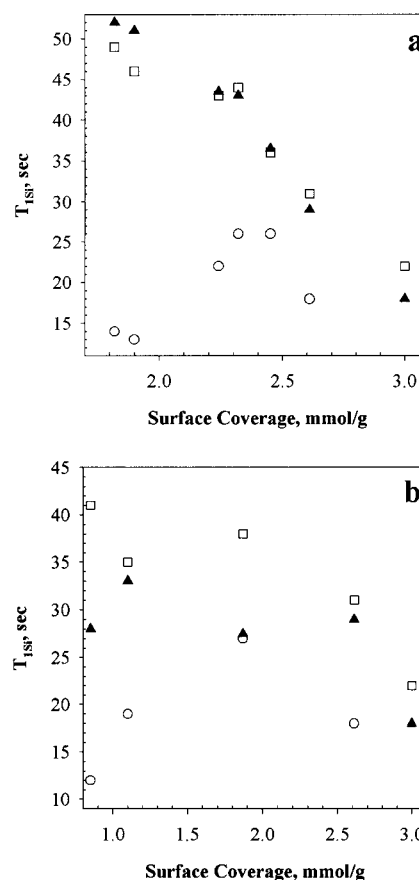

Figure 10. Relation between the surface coverage and the longitudinal relaxation time T_1 for different silicon sites, monofunctionally attached silane M (○), silanols Q^3 (▲), and siloxanes Q^4 (□), in the samples of the FSM-16 mesoporous material functionalized with (a) ClSiMe$_2$R silanes and (b) ClSiR$_3$ silanes. Estimated error: ±10%.

surface coverage for both ligand's series, but after a certain concentration T_1 starts to decrease despite the fact that surface coverages for such samples are even lower. The bell-like shape of the plot of the relaxation time vs surface coverage (Figure 10) for M sites can be partially explained by increasing amount of water and unreacted surface silanols present in the sample with a low ligand coverage (higher number of relaxation sources). T_1 relaxation times for Q^3 sites resemble those for Q^4, and they are similar. T_1 values for Q^4 and Q^3 are only slightly different for the samples modified with SiMe$_2$R ligands (Figure 10a). The FSM-16 samples modified with SiR$_3$ silanes have T_1 relaxation times substantially different for Q^4 and Q^3 sites (Figure 10b). T_1 for Q^3 sites of the modified samples increases up to 28−33 s and is almost constant for all samples modified with trialkylsilanes −SiR$_3$. On the other hand T_1 for Q^4 sites gradually increases from 22 to 35−40 s. Such behavior of relaxation times for the samples modified with ClSiR$_3$ silanes as well as longer relaxation times for the samples modified with longer ClSiMe$_2$R silanes can be interpreted by the difference in the accessibility of Q^3 and Q^4 sites for water molecules as well as for molecular oxygen which can serve as relaxation sources for these sites in the samples that do not have a densely packed ligand layer.

Comparison of longitudinal relaxation times T_1 with results published for conventional silicas (unmodified and modified)[59] and mesoporous materials[60] makes it possible to conclude several points. First of all, FSM-16 material and samples modified with monochloroalkylsilanes are very similar to conventional silica in terms of the longitudinal relaxation time

T_1 for different silicon sites. Second, some differences in the relaxation times for the pure mesoporous material[60] apparently manifest differences in the preparation procedures, the extent of the sample's hydration, and the amount of surface silanols.

4. Conclusions

A detailed study of FSM-16 mesoporous material, as a model of silica surface, and its interaction with alkylsilanes has shown the great complexity of such a process. The results of high-resolution TGA, ^{29}Si NMR spectroscopy, and adsorption measurements are consistent with the interpretation that the process of modification includes several steps. The first phase includes interaction of silane molecules with the surface, and the final step in this process is related to the conformational changes. TGA and ^{29}Si NMR studies revealed that approximately half of available silanols are isolated. Not all present silanols can be functionalized by alkylchlorosilanes. The main reason for this is a close location of surface hydroxyls and possible wall's curvature of mesoporous materials. It was found that, in the case of grafting alkyl ligands on the silica surface of the FSM-16 material, initially silanes with longer alkyl chains exhibit more disordered structure of the surface layer than short alkyl chains, but upon storage or thermal treatment an improvement in their ordering was observed. Alkyl phases with high ordering of attached ligands exhibit decomposition at much higher temperature. The fact that the mesoporous structure of FSM-16 was preserved during the functionalization procedure and that modified samples had narrow pore size distributions makes it possible to adjust the pore diameter of FSM-16 (in the range 2.6−3.3 nm for the starting 3.7 nm material) by varying size of ligands. Studies of longitudinal relaxation times T_1 for ^{29}Si showed a similarity between FSM-16 and amorphous silica. Nitrogen adsorption and NMR measurements as well as adsorption energy distributions revealed greater accessibility of the silica surface of FSM-16 material modified with small ligands in comparison to longer one. The obtained results show that with increasing length of ligands another factor starts to play a significant role, i.e., ordering of long alkyl chains on the surface and its screening not only due to the attachment of ligands but also due to the physical coverage of the surface by long and bulky alkyl groups. The fact of physical coverage of the surface by nonpolar alkyl chains is clearly visible for mesoporous materials modified with large octadecyldimethylsilane.[54] In this case nitrogen molecules more strongly interact with the surface because of relatively low concentration of the ligand, which does not cover the surface completely indicating an island structure of the phase.[54] Such geometrical factors increase chances for appearance of uncovered areas of residual silanols especially during the first step of functionalization by means of modifiers with longer alkyl chains or trialkylsilanes. The screening effect and different density of ligand packing on the surface contribute to several observed phenomena, which need to be considered in potential applications of these materials in adsorption, chromatography, and catalysis.

Supporting Information Available: Figures showing TG and DTG curves for unmodified FSM-16 and the sample exposed to water vapor, TG and DTG curves for samples functionalized with octyldimethylsilane from different solvents, the relationship between the surface coverage and the number of carbon atoms in attached ligands, and nitrogen adsorption isotherms and adsorption energy distributions for samples functionalized with trialkylchlorosilanes (3 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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