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Direct Method for Surface Silyl Functionalization of Mesoporous Silica

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A direct method of surface silyl modification and simultaneous surfactant removal of mesoporous silica is investigated in its physicochemical details. Twelve different silanes of various functionalities are studied. The method employs an alcohol solution of silanes to allow the simultaneous surfactant/silyl exchange process, which results in a more uniform monolayer coverage of the surface and a higher amount of surface attachments of silane. We vary the solution concentration of silanes to study the effect on loadings. It is found that the variation of the surface loading of the silyl group follows a Langmuir adsorption model closely. The method gives one a well-controlled monolayer coverage of the surface. The loadings are determined by the exchange equilibrium. Fittings of the loading data to Langmuir adsorption isotherms give one the adsorption equilibrium constants and maximum surface loadings. We categorize the silanes into three different groups according to the values of the equilibrium constants and discuss them with respect to molecular structures. We also report on the extensive characterizations of the surface-functionalized mesoporous materials, such as nitrogen adsorptions, X-ray diffraction, ^{29}Si magic-angle spinning NMR, ^{13}C magic-angle spinning NMR, and IR spectroscopy. The method provides one with a convenient and highly controllable approach to the surface functionalization of mesoporous silica.

1. Introduction

The synthesis of mesoporous silica is an active field of research in materials chemistry. Surface functionalization with silanes further achieves materials with desired surface properties for applications in catalysis and adsorption. Various functionalities, such as metal complexes or acid or base groups, can be introduced onto the surface by proper choices of functional groups.[1] At the same time, a growing number of organized assemblies and host systems have been used as nanoreactors.[2] Mesoporous silica with tailor-made surface functionality would be a versatile nanoreactor system where chemical reaction can be confined and compartmentized.[2] Reactions in which molecules are physically constrained could lead to much new fundamental understanding of the use of the local environment to control chemical reactions.[3] Mesoporous silica with designed surface functionality would be an excellent nanoreactor.

Periodic mesoporous silicas may be readily synthesized under a wide range of pHs from acidic to basic conditions and at the temperature range from subambient to hydrothermal temperature by using cationic, anionic, neutral, zwitterionic, bolaamphiphile, gemini, and divalent surfactants and a variety of commercially available copolymers, respectively.[4] Numerous new mesophases were also discovered.[5] Examples are SBA-1($Pm\bar{3}n$) and SBA-6 ($Pm3n$), SBA-2[5b] and SBA-12 ($P6_3/mmc$),[5c] SBA-16 ($Im3m$),[5d] SBA-15 ($p6mm$),[5e] and MSU-n.[5f] There are plenty of choices of channel sizes and structures for the construction of nanoreactors.

Chemical surface modification of periodic mesoporous silicas via covalent bonding of organic molecules has been achieved by using two general strategies. The postsynthesis grafting procedure is often the method of choice since the early development of mesoporous silica. Co-condensation procedures, on the other hand, as developed by Burkett et al.,[6a] Pinnavaia et al.,[6b−d] Ozin et al.,[6e−g] Burleigh et al.,[6h] and others,[6i,j] are also popular because they are simple and often give higher loading. However, the co-condensation method has the uncertainty that the functional organosilanes may not be completely attached on the surface and there may be phase separation at high

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loadings. Therefore, quantitative control of loadings may not be simple in the co-condensation approach.

In postsynthesis functionalization,[7] it is often desirable to start with a large number of surface silanol groups (Si−OH) on the mesoporous silica wall after the removal of the surfactants when a high surface coverage of functional groups is preferred. However, high-temperature calcination is usually preceded before functionalization in standard methods. This would lead to more surface silanol condensation and reduce the Si−OH density for the subsequent surface modification.[8] While one can recover the surface silanols by adding a trace amount of water,[9] the procedure becomes complicated and difficult to control. Moreover, excess water will also cause self-condensation of the silanes among themselves. Besides, calcination wastes the expensive surfactants of quaternary ammonium.

Recently, several laboratories have developed methods of surface functionalization with simultaneous extraction of the surfactant and grafting of organic functionalities without prior calcination.[10,11] This type of approach was reported by Antochshuk et al. on MCM-41 and Ce-MCM-41 by using organosilanes as solvents and modifying agents at the same time.[10] They showed that the displacement reaction was possible if the organosilane exhibits at least one reactive group such as Cl−Si, EtO−Si, or MeO−Si. By working on acid-synthesized mesoporous silica, we recently achieved simultaneous extraction of surfactant and grafting of silanes by using alcohol as the solvent. We named this as the direct method of surface functionalization. According to Lin et al.,[11] the surfactant−silyl exchange process is greatly favored when applied to mesoporous silica prepared under acidic conditions because of the weaker interactions between the silica walls and the surfactants compared to those in materials prepared under basic conditions. Acid-made MMS is believed to possess more abundant silanol groups. For example, the surface density of Si−OH groups of folded-sheet mesoporous material (FSM) silicates made from C_{18}TMA is around 3.6 groups/nm^2 after extraction in ethanol solution.[7c] For MCM-41 synthesized via the basic route, the silanol density is commonly believed to be less than 3.0 groups/nm^2. We have found that by using alkylchloro- and alkoxysilanes higher ligand loadings (1.98−2.93 groups/g) can be achieved easily in ethanol solution under milder reaction conditions (50−70 °C; 1−3 h).[11]

Table 1. Physicochemical Properties of CTS Functionalized on Mesoporous Silicas by the Direct and Two-Step Post-Synthesis Procedures[a]

silica mesophase	solvent	d_{100} (nm)	*G* (mmol/g SiO_2)	α (nm^{-2})	PSD (nm)	S_{BET} (m^2/g)
NMMS		4.2			3.2	1084
as-synthesized	ethanol	4.3	3.40	1.88	2.8	866
extraction	toluene	4.3	2.77	1.54	3.0	876
calcination	ethanol	4.1	2.40	1.33	2.3	953
calcination	toluene	4.2	0.789	0.44	2.7	954
MCM-41		4.3			2.9	1005
acidification	ethanol	4.5	2.42	1.45	2.5	763
extraction	toluene	4.5	1.87	1.12	2.5	872
calcination	ethanol	4.5	2.02	1.21	2.5	619
calcination	toluene	4.4	2.33	1.40	2.4	734

[a] The concentrations were controlled at 0.31 M relative to 1.0 g of NMMS.

After our initial report of the direct method, we made a further detailed study of the process over many different supports and silane species. And it is found that the direct method is a well-controlled process. The loading of surface silane, depending on the solution concentration of the silane, can be sub-to-monolayer by control. In contrast to other methods, the amount of loading seems to be determined by equilibrium thermodynamics in the direct method. The surfactant−silane displacement reaction can be modeled by a surface adsorption-like equilibrium process. It is the purpose of this paper to report a detailed physicochemical study of the direct surface functionalization. The surface loadings of each silane on acid-made mesoporous silica were studied with respect to concentration, time, and temperature. The maximum loading of each silane on mesoporous silica was also investigated for the direct method.

2. Experiment Section

2.1. Synthesis of the Mesoporous Materials. The MMSs obtained via the acid route were synthesized according to previous report.[12] The amphiphilic template is trimethylstearylammonium chloride (C_{18}TMACl) from Tokyo Chemical Industry. These organic surfactants were dissolved with the proper amount of water followed by addition of inorganic acid, such as HNO_3. Then, tetraethyl orthosilicate (TEOS, 98%, Acrôs) was inducted into the gel solution at 40 °C until the stirred solution was clear. The solid product was recovered by filtration, washing with deionized water, and drying at ambient temperature or 100 °C.

The direct method of functionalization can also be applied to alkaline-made mesoporous silica, MCM-41 material, after pre-acidification. The interaction between the surfactant and the silica may be reduced in the acid solution.[13] A total of 1.0 g of as-synthesized MCM-41 was stirred in 50 g of nitric acid solution, where the pH was controlled around 0 at room or a lower temperature for 1 day (nanostructure will be retained and the chemical composition is identical). The acidified MCM-41, with a weaker interaction between the silica and the surfactant ($I^0\cdots NO_3^-C_{18}TMA^+$) is then suitable for the direct surface modification process.

2.2. "Direct Silane Modification" of the Uncalcined Acid-Made Mesoporous Silicas and the Acidified MCM-41. A total of 1.0 g of as-synthesized MMS (SiO_2, 48.62% based on elemental analysis) or acidified MCM-41 and a desired amount of silane sources, as listed in Table 1, were soaked together in 50.0 g of an ethanol (99.5%) solution. The moles of silanes relative to 1.0 g of MMS in the solution are in the range of 1−30 mmol.

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Then, the mixtures were refluxed for 1−3 h. The modified MMS was recovered by filtration, washed with ethanol several times, and dried at 100 °C. The quaternary ammonium surfactant may be separated from the ethanol solution and recovered by evaporation under the reduced pressure.

2.3. Loadings Calculation of Surface Grafting. The amount of loading after surface functionalization was determined by elemental analysis. According to the elemental contents (C/H/N/S) of the silylated products, the loadings of the grafted groups (Γ) for all the silylated materials were calculated in the unit of millimole per gram of pure silica (mmol/g SiO_2).[8a]

$$\Gamma = \frac{\Delta W_i\% \times 1000}{\Delta W_{SiO_2}\% \times nM_i} \quad \text{mmol/g SiO}_2 \tag{1}$$

ΔW_{SiO_2} represents the inorganic SiO_2 contents in weight percent. And ΔW_i (i = C, N, S) is the weight percents of carbon, nitrogen, or sulfur in which M_i is its corresponding atomic weight and "n" is the number of the corresponding atoms in one molecule of the silane. For alkylchlorosilanes without carbon interference from alkoxyl groups, such as chlorotrimethylsilane (CTS) and bromomethyldimethylchlorosilane (BDCS), the loadings are based on carbon contents. For silanes with functional groups, such as amine and thio, the heteroatoms are available; in that, the loadings are calculated from the nitrogen or sulfur contents instead of the carbon contents. For alkoxysilanes, the unhydrolyzed RO group will give interference to the carbon content and, thus, the surface coverage based on the carbon content is unreliable. Hence, we calculated the ligand loadings with the nitrogen or sulfur content of aminosilanes, mercaptosilane, and cyanosilane. For the alkoxysilanes without organic functionalities, we used chlorosilanes instead of alkoxysilanes to avoid any ambiguities in the evaluation of the ligand loading. In our study, the displacement of the surfactant template is mostly complete and the percentage of residual surfactants, checked by elemental content, is always less than 3%.[14]

The surface density (α) of loaded functional groups can be calculated from the following eq 2, (N_A is Avogadro's number and S_{BET} is the surface area):

$$\alpha = \frac{\Gamma N_A}{1000 S_{BET}} \times 10^{-20} \quad \text{groups/nm}^2 \tag{2}$$

2.4. Characterization. The powder X-ray diffraction (XRD) patterns of the modified MMS samples were collected on a Scintag X1 diffractometer (Cu Kα = 0.154 nm) within the 2θ range of 1.5−8°. Nitrogen adsorption−desorption isotherms of the samples were obtained on a Micromeritics ASAP 2010 system at 77 K. The specific surface areas were calculated by using the BET model (P/P_0 = 0.05−0.25). And the pore size distribution (PSD) was obtained from the analysis of the adsorption branch by using the Barrett−Joyner−Halenda method. ^{13}C (75.43 MHz) and ^{29}Si (59.63 MHz) magic-angle spinning (MAS) NMR experiments were performed at room temperature on a Brüker MSL 300P NMR spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG209 thermogravimetric analyzer to measure the surfactant and organic composition contents of the modified mesoporous silicas. The IR spectra were recorded on a MAGNA-IR 500 spectrometer in the range of 400−4000 cm^{-1} by using the KBr pellets technique (sample/KBr = 1:20), with a scan number of 32 and a resolution of 4 cm^{-1}. The C/H/N/S amounts of the modified mesoporous silica were determined by the 2400 Π element analyzer of Perkin-Elmer and Heraeus.[16]

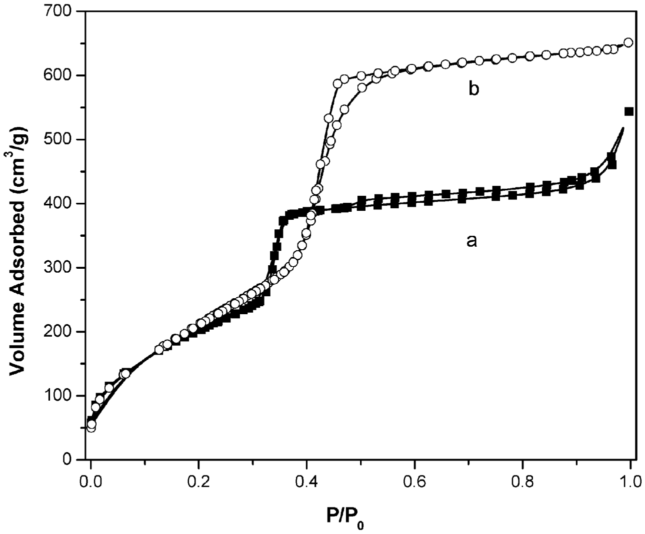

Figure 1. N_2 adsorption−desorption isotherms of (a) HNO_3- and (b) HBr-made MMS after silylation of CTS by the direct modification.

2.5. Chemical Abbreviations. In this work, a large number of organosilanes as grafting agents are studied. We use their abbreviated names throughout the paper. They are listed as follows. Micelle-templated mesoporous silicas (MMS). Nitric acid-made micelle-templated mesoporous silicas (NMMS). Silanes: chlorotrimethylsilane (CTS); bromomethyldimethylchlorosilane (BDCS); *tert*-butyltrichlorosilane (TBTCS); *tert*-butyldimethylchlorosilane (TBDMSC); 3-mercaptopropytriethoxysilane (MPTS); 2-(diphenylphosphino)ethyltriethoxysilane (DPETS); 3-trimethoxysilylpropyl chloride (TSPC); 3-aminopropyltrimethoxysilane (APTS); *N*-methylaminopropyltrimethoxysilane (MAPTS); *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPTS); 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTS); and 3-cyanopropyltrichlorosilane (CPTS).

3. Results and Discussion

In this section, we first discuss the main factors that affect the results of surface functionalization, including counterions, concentration of silanes, and temperature. We will also compare the results with those obtained from the conventional calcination/graft approach. We have performed experiments for all the silanes listed in the experimental section. However, for the purpose of illustration and comparison, we will mostly present the case of using CTS to obtain trimethylsilyl (TMS) functionality in detail.

3.1. Effect of the Counterion. Because in acid-made MMS the counterion (X^-) participates in the binding of the surfactant ion (S^+) on the silica through the interaction $S^+X^-I^0$,[12d] the kind of X^- species from the acid (HX) will affect the degree of surface functionalization. We first examine this effect by comparing the extent of surface modification of CTS on two different MMS samples synthesized in HNO_3 and HBr solutions, respectively. The surface area (PSD) of HNO_3- and HBr-made MMS after acid extraction in ethanol are 1044 m^2/g (3.4 nm) and 995 m^2/g (3.5 nm), respectively. Under the same concentration of CTS and procedure, direct silylation of mesoporous silicas made from the two different acids (HNO_3 and HBr) result in different loadings of TMS (2.49 and 2.05 mmol/g SiO_2) and pore volumes (0.64 cm^3/g and 0.81 cm^3/g). From the N_2 adsorption−desorption isotherms (Figure 1) and the PSDs, we found that the HBr-made MMS after CTS silylation possesses a larger pore volume and pore size (2.8 nm) than the HNO_3-made MMS (2.5 nm). It is consistent with less loading of TMS groups on HBr-made MMS.

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[14] The nitrogen contents of parent and modified NMMS are 3.0% and below 0.1%, respectively. Because the precision of the elemental analyzer (Perkin-Elmer 2400) is also limited to 0.1%, the residual nitrogen content of modified NMMS is at most 3.3% from the quaternary ammonium.

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[16] The anionic effects on mesoporous silica synthesis are reviewed recently in connection with the Hofmeister series of anions; see Leontidis, E. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 81.

The silane modification processes may be regarded as an interfacial reaction, as in the following scheme:

$$\equiv\mathrm{Si{-}OH\ X^-\ C_{18}TMA^+ + Cl{-}SiR_3} \rightleftharpoons$$
$$\equiv\mathrm{Si{-}O{-}SiR_3 + C_{18}TMA^+X^- + H^+ + Cl^-}$$

A stronger binding counterion X^- would make the chemical potential of solution species $C_{18}TMA^+X^-$ lower, and the above equilibrium would shift more toward the right-hand side. Previously, we have shown that the strength of binding of the counterion X^- in the as-synthesized MMS follows the well-known Hofmeister series[15] that ranks the anions in the order of $Cl^- > Br^- > NO_3^-$ in dissociating from the surfactant.[16] If the interaction between $C_{18}TMA^+$ and X^- is strong (as in NO_3^-), the hydrogen bonding between Si−OH and X^- is relatively weakened. Then, the templates are easily extracted from mesopores and the silanes can be more easily exchanged onto the silica surface. Compared to nitrate, Br^-S^+ is less easy to extract in that the surface Si−OH group is more shielded and the degree of silylation thus decreases. For comparison, we always use NMMS synthesized with nitric acid as the acid source and $C_{18}TMACl$ as the template. For the purpose of application, the morphology of NMMS is in long ropes[17] and the use of NMMS also has the advantage of resulting in higher functionalization because the nitrate ion is one of the strongest binding counterions to surfactants.

3.2. Comparison of Surface Modification Methods. In this section, we compare the direct method of functionalization of CTS with the corresponding two conventional methods: on calcined or extracted mesoporous silica. The results are listed in Table 1. In either conventional method, functionalization is performed on surfactant-removed MMS.

In the calcinations method, the MMS was first treated at 560 °C under air for 6 h to remove all the surfactants. In the extraction method, the templates are extracted in acidic ethanol to preserve the abundant surface silanol groups. In addition, mesoporous silica after extraction must be heated under a vacuum to remove the adsorbed water or residue acids, for hydrogen-bonded (HB) silanol is inactive for surface modification.[18] Generally speaking, XRD patterns of the hexagonal mesophase are preserved in both processes.

The direct modification approach on uncalcined NMMS can be performed under mild conditions in a single step where the surfactants are extracted and the silanes are grafted simultaneously. The absence of the NO_3^- characteristic peak for modified NMMS at the 1350−1390-cm^{-1} IR region[11a] provides a direct evidence that most templates ($C_{18}TMA^+NO_3^-$) are displaced by organosilanes. The residual templates were found to be less than 3.3%, as elucidated by the nitrogen content.[14] For MMS, we note that ethanol is a better solvent for the exchange reaction (Table 1) to introduce more silanes onto the hydrophilic silica surface. At the same concentration of CTS in ethanol, the loadings of TMS groups by the direct method on NMMS are higher (3.40 mmol/g SiO_2) than those by the conventional procedure on the calcined one (2.40 mmol/g SiO_2). On the other hand, we have found that the PSD of NMMS by the conventional modification method (2.7 nm) is about the same as that by the direct method (2.8 nm).

It is known that the adsorbed water in calcined MMS usually leads to a nonuniform grafting and pore constrictions upon surface modification. A uniform surface functionalization characterized by a sharp gas adsorption curve is desirable. Figure S1 gives the PSDs of four representative samples (CTS, BDCS, APTS, and MPTS) functionalized by the direct method. The sharp capillary nitrogen adsorption curves are almost parallel to the blank-extracted mesoporous material with little shift to smaller relative pressure. The PSDs show narrow widths of about 0.5 nm. This indicates a pretty uniform surface coverage of the channel wall. Usually, a moisture-free condition and dried solvent is necessary for a well-controlled modification on calcined surfactant-free mesoporous samples.[19] However, in our direct method with the surfactants occluded inside the nanochannels, adsorption of water from the atmosphere is prevented. Thus, this unique advantage makes a homogeneous silane modification easily achieved.

Table 2. Silylation of CTS on NMMS at Different Temperatures and Reaction Times[a]

temperature (°C)	time (h)	C%	N%	Γ (mmol/g SiO_2)
25	24	11.58	0.21	2.69
40	24	11.60	0.22	2.67
78	0.5	8.77	0.0	2.75
78	1.0	9.17	0.05	2.89
78	1.5	9.96	0.0	3.18
78	4.0	9.35	0.03	3.06

[a] The concentrations of CTS are controlled at 0.17 M.

The other factors in controlling grafting are the reaction time and the temperature. The samples silyated at 25, 40, and 78 °C are analyzed and shown in Table 2. The longer the reaction time and the higher the reaction temperature are, the higher is the loading of grafting. At about 1.5 h for the case of CTS at 78 °C, it reaches saturation. This is probably in equilibrium. Hereafter, we study mostly the degree of silylation at a long enough reaction time where it depends on the equilibrium concentration of silanes. Also, the temperature dependence of loading is small, indicating an exchange reaction that is small in enthalpy change. This is in contrast to the large exothermicity during the displacement modification in the study of Antochshuk et al.,[10c] where a stronger driving force is expected with the silanes as the solvent.

APTS is a popular and useful silane with an amine functional group not only for its amino functionality for metal ion chelating agents but also for advanced heterogenized catalysis, such as in the Knoevenagel reaction.[1a] Hence, it is desirable to get a high loading of APTS functionality. Comparisons of direct APTS modification with the conventional method are given in Supporting Information. According to the literature,[1,7c,10a] the loadings of APTS amino moieties grafted on mesoporous materials by traditional methods are between 1.2 and 1.7 groups/nm^2 (see Table S1) on the different silica substrates. In this study, a high loading (1.95 groups/nm^2) and high surface area (810 m^2/g) can be simultaneously achieved by the single-step modification in the silane/ethanol solution.

3.3. Acidification of Alkaline-Made MMS. For alkaline-synthesized MMS, such as MCM-41 and MCM-48, the electrostatic interaction between the surfactants and the silica wall ($C_{18}TMA^+I^-$) is stronger than those in acid-made MMS ($C_{18}TMA^+X^-\cdots I^0$). Hence, Jaroniec et al.[10] resorted to using the silanes as the solvent to provide a stronger driving force for their surface modification. But

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(19) There are several studies showing that grafting takes place mainly on the relatively more hydrophobic portion of the TMS surface. See, for example, Bellocq, N.; Abramson, S.; Laspéras, M.; Brunel, D.; Moreau, P. *Tetrahedron: Asymmetry* **1999**, *10*, 3229.

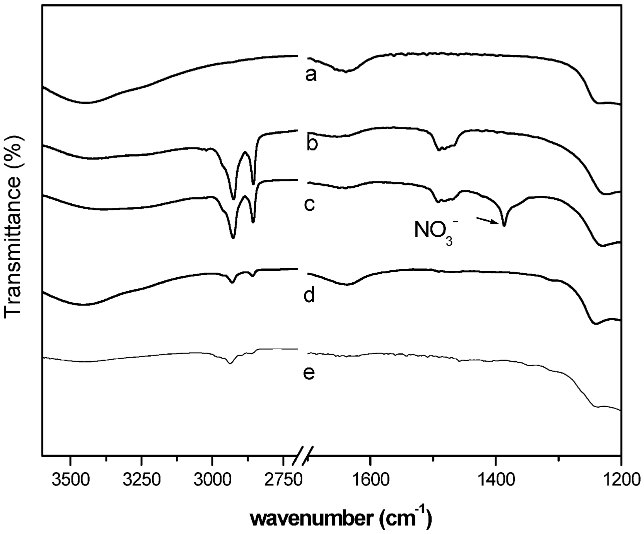

Figure 2. Fourier transform infrared spectrum of MCM-41 (a) after calcination, (b) as-synthesized, (c) after HNO_3 acidification, and after functionalization with (d) MPTS and (e) CTS silanes.

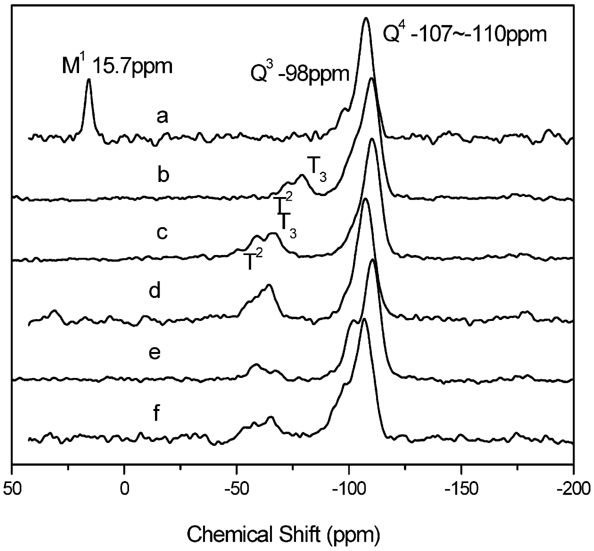

Figure 3. ^{29}Si MAS solid NMR of NMMS after silylation of (a) CTS, (b) PTES, (c) TSPC, (d) MPTS, (e) CPTS, and (f) APTS. Chemical shifts are reported relative to TMS.

it is wasteful and inefficient; it needs more silanes and takes twice as much time to completely remove surfactants. In our solvent system, we can simply transform the strong electrostatic interactions (S^+I^-) of MCM-41 samples into a weak hydrogen-bonding form ($C_{18}TMA^+X^-\cdots I^0$) via an acidification (pH < 1) treatment procedure.[15] Then, we follow with the silane replacement reaction as in the aforementioned alcoholic solution.

The dried, as-synthesized MCM-41 or MCM-48 samples were treated with a strong acid solution (pH < 1).[13] Elemental analyses of the treated samples show that the nitrogen content (3.0%) of acidified MCM-41 almost doubled that of the parent MCM-41 sample (1.60%). This implies that the NO_3^- ion is incorporated in a nearly 1:1 ratio to the surfactant cation. To understand the interaction transformation of the mesoporous surfactants−silicas composites, we systematically compared the IR spectra of the MCM-41 mesoporous silicas before and after nitric acid solution treatment (Figure 2). There is also an additional strong absorption in the IR spectrum in the range of 1350−1390 cm^{-1}, which is due to the N−O stretching vibration of nitrate ions. Thus, we believe that we have transformed the silica−surfactant interaction to those in acid-synthesized mesoporous silica, such as in NMMS.

We first compare the loadings of TMS groups by the two kinds of pretreatment methods, acidification and calcination procedures, prior to MCM-41 modification (Table 1). The acid-treated MCM-41 in the direct silane/ethanol process shows the highest TMS loading (2.42 mmol/g SiO_2) while the acid-extracted MCM-41 will give the lowest loading (1.87 mmol/g SiO_2) by the conventional silane/toluene process.

Then, we also compare the loadings of TMS groups by our direct silane/ethanol process with the two kinds of mesoporous silica, acid-treated MCM-41 and as-synthesized NMMS. For as-synthesized NMMS, the one-step process shows the highest TMS loading (3.40 mmol/g SiO_2) among all the samples, much higher than the acid-treated MCM-41 (2.42 mmol/g SiO_2). This is mainly due to less silanol abundance in MCM-41 than in NMMS.

3.4. Characterization of Organic Moieties on Mesoporous Silica. In this section, we report the characterization of the functionalized moiety by thermal and spectroscopic techniques. TGA is performed to identify the organic contents. TGA data of silylated-synthesized NMMS are given in Figure S2 of Supporting Information. The surfactant residues and nitrate ions can also be checked by the corresponding IR absorption bands.[11a,13] Mesoporous silica materials containing monolayer organic moieties have been evaluated by using ^{13}C and ^{29}Si MAS NMR. The ^{29}Si MAS NMR spectrum (Figure 3) of modified NMMS is similar to those previous reports for modified MCM-41[10a] or FSM-16.[7c] For the parent NMMS, intensities of the peaks at −98 and −110 ppm, corresponding to the silanol (Q^3) and siloxane (Q^4) sites, are almost equal while geminal silanols Q^2 (signal at ca. −89 ppm) exist in a relative minor amount of 5% or less.[15a] According to Zhao and Lu,[18] single (Q^3) and geminal silanol (Q^2) groups are active for silylation but HB silanols are not because of the hydrophilic networks formed among them. Although the HB silanols cannot be distinguished by ^{29}Si NMR, they can be observed by ^1H NMR[22,23] or IR.[24] In the ^{29}Si NMR spectrum, conventional notation M^n and T^n were designated to the different silicate species on the basis of the number of carbon and oxygen bridging atoms in which the n index represents the number of oxo bridges. CTS possesses only one hydrolyzable group, herein M^1 is observed sharply at 15.7 ppm on the ^{29}Si NMR spectrum.[10d,18,20] For trialkoxyl silanes, siloxane groups functionalized on the silica surface are classified into three different species:[7a] (i) isolated groups T^1 (−49 ppm), (ii) terminal groups T^2 (−58 ppm), and (iii) cross-linked groups (−66 ppm). At a higher coverage, the attached molecules are closer to one another to form a cross-linked monolayer and the isolated siloxane groups (T^1) are sparse (Figure 3). The signals of T^2 and T^3 are usually the main components.[22] And T^3 will dominate when the coverage is close to monolayer[7a] as the loading of organosilanes is increased.

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Moreover, the functional groups will partially affect the chemical environment of Si attached to the silica surface. For example, the ^{29}Si spectrum of PTES-modified silica shows upper fields of T^2 (−72 ppm) and T^3 (−78 ppm) than other trialkoxyl silanes, such as CPTS, TSPC, MPTS, and APTS. This is mainly because the spatial de-shielding from the phenyl ring attached to the T^3 or T^2 silicon.[23] Moreover, according to Smaihi and Jermoumi, the chemical shift of the T^3 species will vary in the range of −79 to −77 ppm. This shift is induced by the changes of the Si−O−Si bond angle as the PTES loading is increased.[25]

There are several signals in the ^{13}C NMR spectrum elucidating the different environments for carbon (Figure 4). Chemical shifts from 0 to 250 ppm are similar to those of pure organosilanes in solution but with broader peaks as a result of characteristics of the solid-state NMR. Caravajal et al.[22a] had suggested that the averaged number of unreacted ethoxyl groups per attached silane moieties (APTS) was between 1.4 and 1.6 as determined by ^{13}C solid-state NMR. In our samples, the position of peaks at 28 ppm (Figure 4b) shows that methoxy groups are not totally hydrolyzed under the displacement condition.

Moisture stability is always a concern in the long-term storage of mesoporous silica. Often the adsorbed water would destroy the structure of the amorphous silica wall.[21] The thinner walls and looser silica structure of MCM-41 make it fragile in boiling water. But after silylation, the acid-made mesoporous silica can generally survive in boiling water for at least half a day and, when stored under ambient conditions, for 1 year, except for aminosilanes. The exception implies that hydrophilic amino groups will not only introduce more water from the atmosphere but also continuously cause the silicon to become more nucleophilic and easily attacked by water.[22,26,27]

3.5. Silane Adsorption Isotherm. The grafting of organosilanes can be regarded as an adsorption−displacement process on the surface of the mesoporous silica in a multicomponent system of surface−solution equilibrium. An adsorption isotherm would be a fundamental way to describe the equilibrium thermodynamics and monolayer limitation of solid/liquid (or gas/solid) distributions, in which the equilibrium concentration of solute in solution, C_{eq}, varies the adsorption ligand loadings Γ (millimoles of organosilane per gram of pure silica). Previously, Ossenkamp et al.[28] had studied the esterification of the silica surface by alcohols. They found that the loadings of alkoxyl groups on silica can be described by the Langmuir adsorption model, which allows the precise control of surface coverage. However, for the silylation of mesoporous silica, there has not been any study on its adsorption isotherm.

In our study, the temperature was maintained at the boiling point of the ethanol solution (78 °C) during the adsorption−displacement process. We vary the solution concentration of silanes to correlate with the degree of surface functionalization. We have collected 11 isotherm data points from the 12 silanes we studied in this work except cyanosilanes. In this study, we focused both on the monolayer coverage of saturated silylation on mesoporous silica and on the equilibrium constants (K) at low coverage. This will help us to reveal the nature of the interaction between the silanes and surface silanols and to gain control over the surface coverage.

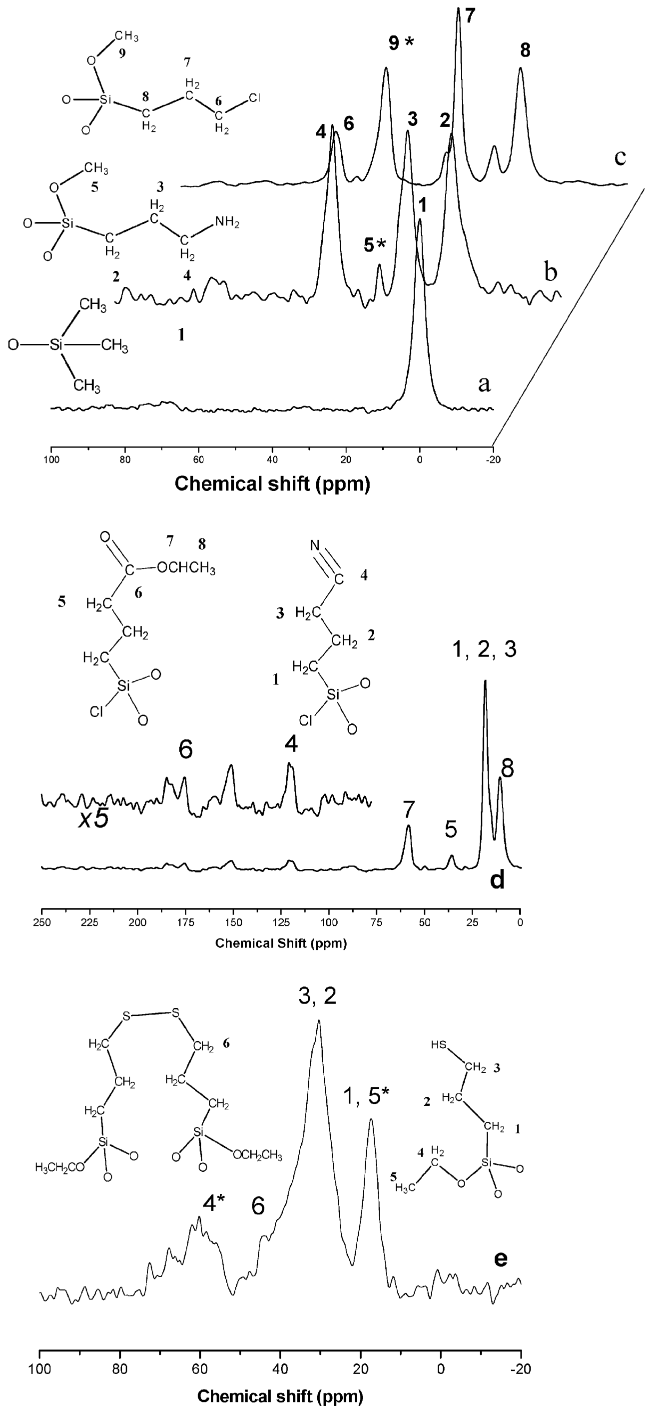

Figure 4. ^{13}C MAS solid NMR of NMMS after silylation of (a) CTS, (b) APTS, (c) TSPC, (d) CPTS, and (e) MPTS. Chemical shifts are reported relative to the TMS. The signals of ethoxy or methoxy groups are marked with asterisks, and the residual surfactants are too few to be observed.

Γ is the loading of adsorbents per gram of solid. Some detailed physicochemical properties, including surface areas, pore sizes, loadings, and coverages, are listed in the Table 3. For each silane, we list the loading data for one or two different silane concentrations, one at high concentration (HC) and the other at lower concentration (LC). One can see that the sample modified at a higher

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Table 3. Physicochemical Properties of Silane-A, Silane-B, and Silane-C Silanes Functionalized on Mesoporous Silica (C_{18}TMACl−TEOS−HNO_3−H_2O) by the Direct Modification Procedure[a]

silane	silane [mM]	C%	Γ (mmol/g SiO_2)	α (nm^{-2})	S_{BET} (m^2/g)	PSD (nm)	coverage (θ)
CTS							
LC	46.9	6.79	1.35	0.75	930	3.1	32.3%
HC	627	11.1	3.57	1.98	792	2.7	85.6%
BDCS							
LC	47.3	5.10	1.73	0.962	1041	2.8	53.9%
HC	322	8.41	2.83	1.81	923	2.7	88.1%
TBTCS	334	7.55	2.33	1.30	873	3.2	64.4%
TBDMS	304	7.85	1.46	0.812	930	3.0	32.7%
MPTS							
LC	77.6	13.62	3.29	1.83	986	3.2	56.6%
HC	378	16.87	5.27	2.93	417	2.0	90.7%
DPETS	379	22.95	1.44	0.800	636	1.8	49.5%
TSPC							
LC	39.4	9.84	3.10	1.72	922	2.6	76.4%
HC	166	12.87	3.93	2.33	746	2.1	96.9%
APTS	201	14.88	3.51	1.95	810	2.5	81.6%
MAPTS	155	12.99	3.04	1.69	654	2.3	82.6%
AAPTS	311	14.43	2.84	1.58	771	2.5	72.3%
AEPTS	181	15.71	2.31	1.28	753	2.4	86.7%

[a] LC: at lower concentration. HC: at higher concentration.

silane concentration always gives a higher surface loading and a smaller pore size. Thus, we decide to systematically vary the silane concentrations to observe effects on the resulting surface loadings. The density of silylation (α), another representation of loading shown in the units of number per squared nanometer, is proportional to Γ and also determined by the concentration of silane in the ethanol solution. This will help us to understand available silanols for modification on the surface and to compare the data in the same units with those of the literature.

When the concentration (C_{eq}) of the silane was varied, the surface coverage (θ) and the ligand loadings (Γ) are calculated from elemental analysis data. In Figure 5, we only show four representative isotherms (CTS, BDCS, MPTS, and APTS) of silylated mesoporous silica from the 11 different silanes we measured. All experiments were carried out with the same relative amount of silica and solvent (1.0 g:50 g) while the concentrations of the silanes were varied systematically. It turns out that Langmuir-like isotherms were obtained. CTS and BDCS reach the monolayer saturation equilibrium at ~0.4 M, while MPTS reaches it at ~0.3 M and APTS reaches it at a much lower concentration below 0.1 M. The equilibrium constant (*K*) and the maximum loading (Γ_{max}) are calculated and obtained from the parameters of the fitting results. These data are analyzed within a concise Langmuir model in which we consider a two-step absorption process is involved. The first step is a physisorption in which the adsorbed molecules are introduced into the nanochannels as the ideal monolayer without interaction with each other. The second step is the chemical bonding formation regarded as an irreversible process.

The siloxane bond formation process is rather slow compared to the physisorption; one may then expect an equilibrium distribution of the physisorbed species.

$$S_{(soln)} \overset{K}{\rightleftharpoons} S_{(surface)} \rightarrow S_{(chemically\ bonded)} \qquad \text{S: silane}$$

Unless the chemically bonded silane species are removed, no further "shift" of $S_{(soln)}$ to the right occurs. The measured product is thus in a one-to-one correspondence

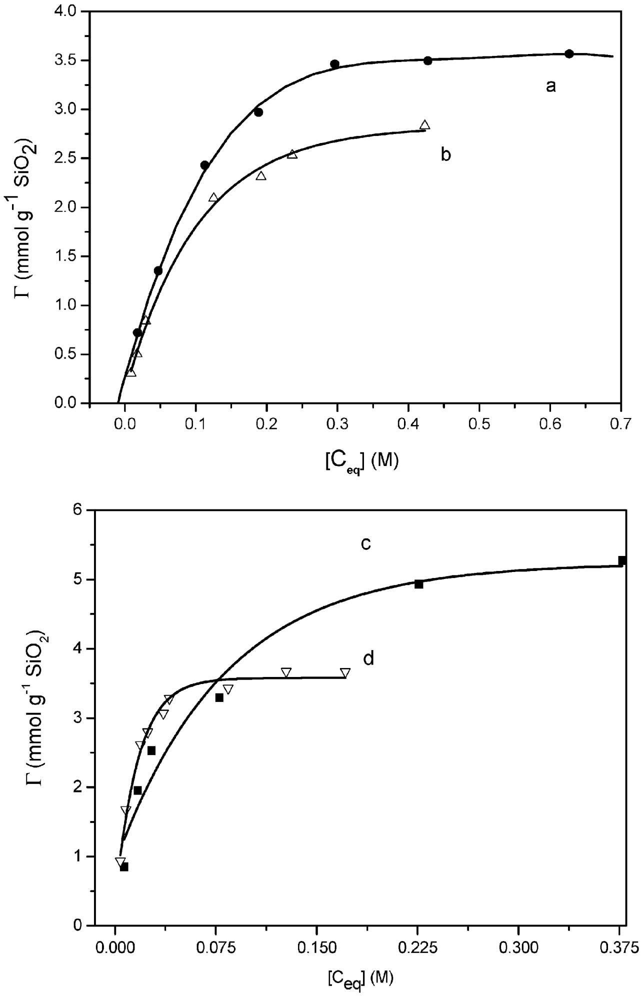

Figure 5. Displacement isotherm of (a) CTS, (b) BDCS, (c) MPTS, and (d) APTS silanes onto HNO_3-made mesoporous silica (NMMS) by the direct modification.

with the physically adsorbed species, which is described by the Langmuir model.

The physisorption process may be described by the familiar Langmuir equation (eq 3).

$$\theta = \frac{\Gamma}{\Gamma_{max}} = \frac{KC_{eq}}{1 + KC_{eq}} \tag{3}$$

In Figure S3, we show four cases (CTS, BDCS, MPTS, APTS) of their fittings of 1/Γ versus 1/C_{eq} closely following with a linear relationship according to eq 4.

$$\frac{1}{\Gamma} = \frac{\Gamma}{\Gamma_{max}} + \frac{1}{\Gamma_{max}KC_{eq}} \tag{4}$$

The use of the Langmuir model here should be carefully qualified. It is the physical adsorption step that controls the surface occupation and, hence, loadings. The second chemical step firmly attaches the adsorbed silanes. The final loading data reflect the extent of physisorption because there is a one-to-one correspondence between the species adsorbed on the surface and the final grafting. This is possible for the chemical grafting reaction where the silane species do not move away from surface to "shift" the equilibrium.

For all of the 11 silanes studied, the fittings of the adsorption isotherms by the Langmuir model (eq 4) are very good. The correlation coefficients are mostly better than 0.99 (see Table 4). Only for the more bulky silanes,

Table 4. Parameters Derived from the Langmuir Absorption Equation at 351 K (78 °C)[a]

silanes	intercept ($1/\Gamma_{max}$)	slope ($1/\Gamma_{max}K$)	K (M^{-1})	Γ_{max} (mmol/g)	α (nm^{-2})	R
CTS	0.2396	0.020 75	11.55	4.17	3.17	0.997 78
BDCS	0.3112	0.025 84	12.04	3.21	2.10	0.996 93
TBTCS	0.2765	0.061 38	4.505	3.62	2.50	0.997 86
TBDMSC	0.2544	0.174 30	1.460	3.93	2.64	0.999 83
MPTS	0.1721	0.006 57	26.19	5.81	N/A	0.996 02
DPETS	0.6185	0.029 30	21.13	1.62	1.53	0.990 74
TSPC	0.2465	0.003 08	80.04	4.06	3.28	0.987 98
APTS	0.2325	0.003 29	70.66	4.30	3.20	0.996 49
MAPTS	0.2715	0.003 28	82.79	3.68	3.39	0.998 60
AAPTS	0.2547	0.003 81	66.84	3.93	3.07	0.998 33
AEPTS	0.3754	0.004 77	78.70	2.66	2.13	0.984 39

[a] *R*: correlation coefficient. N/A: not available.

such as AEPTS and DPTES, the fittings of the absorption curves to Langmuir-type isotherm are not as good, as revealed by the lower correlation coefficient (Table 4). The high precision of the data reflects that the direct modification process is both a robust and a reproducible method, which gives monolayer functionalization at saturation. From the intercept ($1/\Gamma_{max}$) and the slope ($1/\Gamma_{max}K$), equilibrium constants (K) were obtained and are listed in Table 4. We also calculated the maximumn surface density (α)/squared nanometer. The maximum loading (Γ_{max} and α) and equilibrium constant provide us much information about the grafting process. The isotherm of CPTS is not reported because we found the cyano (alkyl nitride) group reacts with the solvent alcohol and changes its nature during grafting, which was inferred by ^{13}C NMR in Figure 4d. That the Langmuir model can fit well the loadings of the silane grafting confirms that the surface modification is monolayer in nature. The high loadings, as shown by the surface density data, indicate that the inner radius of the channel is pretty uniform after surface functionalization.

According to the values of adsorption equilibrium constants, we may categorize the silylation into three groups: silane-A, silane-B, and silane-C. Hydrophobic alkylchlorosilanes (R = methyl, bromomethyl, and *tert*-butyl) belong to silane-A, and their equilibrium constants are less than 20 M^{-1}. Moreover, the equilibrium constants (K) of TBTCS and TBDMSC, due to the hindrance of *tert*-butyl groups, are much lower than those of BDCS and CTS. Because surface silanols are regarded as hydrophilic groups, the hydrophobic silanes are not favorably adsorbed into the nanochannels and a lower equilibrium constant is, thus, observed. Silane-B is the organic silane with thio or phosphine functionalities, and its equilibrium constants (K) are between 20 and 30 M^{-1}. In this group (MPTS and DPETS), both silanes possess somewhat polar functionalities, and equilibrium constants are higher than those of the silane-A group. It seems that both the headgroup (ethoxy) and the tail group (thio or phosphine) contribute to the polarity. The last division of silanes, silane-C, is the one with the amino as the tail group and the methoxy as the headgroup. Their equilibrium constants are mostly above 70 M^{-1}, and they are believed to have strong interactions with the silica surface.[22,26] The interaction between the aminosilane molecule, such as APTS, and the silica surface is through a strong hydrogen bonding complex.[22,26,29] The molecule APTS may interact with surface silanol either by a H bond to the nitrogen atom on amine or to the polar methoxy group. Then, the methoxy groups of the APTS condense irreversibly with surface silanols to form a siloxane bond. As explained before, it is the first step of physical exchange/adsorption that determines the Langmuir behavior. The later irreversible chemical condensation simply fixes the orientated adsorbate onto the surface. We, thus, obtained a Langmuir-like behavior of surface loading. The strong H-bond interactions in silane-C are responsible for higher surface binding constants. For the tail group of chloro in TSPC, a similar H bond of silanol to Cl also probably explains its high equilibrium constant. For multi-amino group silanes, the equilibrium constants are about the same as those of APTS. Take AAPTS with two amine groups, for example; a two-step adsorption in time sequence is found by Impens et al.[26b] In the initial physical adsorption, only one H bond is involved. This explains the equilibrium constants being roughly in the same range as that of APTS. It seems that our data show loadings and the adsorption equilibrium constants are mainly controlled by the weaker physical interactions between the functional group of silane and the surface; thus, it further confirms the two-step reaction scheme. Because of the limitation of available silanes, we are not able to distinguish the relative contributions of the head and tail groups in their interactions with the silica surfaces. Further studies using other kinds of silanes may be desirable.

After silylation of CTS on NMMS, the density of the highest density of silylation (1.98 groups nm^{-2}) and coverage (85.6%) of trimethyl groups is similar to the highest loadings of 85% of MCM-41[18] and 1.7 groups/nm^2 of FSM reported thus far.[7c] The effective molecular area of the TMS group was estimated by assuming that each group occupies a cylindrical volume of space of 0.43 nm^2. The theoretical maximum density of the attached TMS was reported to be about 2.33 groups/nm^2.[30] To our satisfaction, this maximum value is just about what we derived from the Langmuir fitting parameter in Table 4, which is 4.17 mmol/g SiO_2, equivalent to 2.32 groups/nm^2. This value indicates a close packing of TMS groups on the silica surface, and it can be obtained precisely from both the theoretical estimation (2.33 groups/nm^2) and the fittings of experiments (2.32 groups/nm^2). It is thus inferred that the Langmuir model is suitable to describe the surface silylation as a monolayer adsorption. This indicates the effects of the energetic heterogeneity, and lateral interactions are negligible.

During grafting, we chose ethanol as the solvent to extract the surfactant in the nanochannels. One may wonder whether ethanol will react with surface silanol leading to esterification.[31] Previously, Ballard et al.[32] estimated the adsorption constant as $K = 0.15$ for 1-butanol at 391 K. This value is far smaller than the equilibrium constants of alkoxysilane condensed with silanol at 78 °C. (More comparisons of esterification are further discussed in the Supporting Information). Moreover, according to the solid ^{13}C NMR spectrum of CTS in Figure 4a, the peak due to methoxy group around 58 ppm is barely detectable. It is concluded that esterification is not significant under our experiment conditions. Only alcohol of much longer chains can give high enough

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[30] (a) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208. (b) Zhao, X. S.; Lu, G. D.; Whittaker, A. K.; Millar, G. J.; Zhu, H. Y. *J. Phys. Chem. B* **1997**, *101*, 6525.

[31] In esterification, the nonpolar solvent xylene is needed to drive the dehydration. In our silylation process, the silyl functionalization is rapid and effective when using ethanol as the solvent. This is due to the high surfactant solubility. In contrast, the process is slow and ineffective in toluene with low surfactant solubility.

[32] Ballard, C. C.; Broge, E. C.; St. John, D. S.; McWhorter, J. R. *J. Phys. Chem.* **1961**, *65*, 20.

equilibrium constants to compete with silylation (Supporting Information Table S2).

Finally, we should note that our direct method applies to both acid- and alkaline-synthesized mesoporous silica provided that a proper acidification step is done to convert the alkaline-made silica–surfactant interaction into the acidic form at a low temperature. In the acid treatment step of alkaline-synthesized mesoporous silica, there is practically no extraction of surfactants, as shown in Supporting Information Table S3 and Figure S4. So the silylation is a true direct replacement reaction, not a two-step extraction/grafting process. The direct replacement reaction gives one a clean monolayer functionalization, as this paper's extensive data have shown.

4. Conclusions

We have reported a detailed study of a direct, one-step procedure for the surface functionalization of cationic surfactant-templated mesoporous silica. The process gives high loadings of uniform monolayer coverage of silanes. We studied the Langmuir-like behavior of loading isotherms in great detail to show the nature of the monolayer surface functionalization. The adsorption isotherm study also gives one the detailed knowledge of the saturation coverage and equilibrium constants from 11 different silanes. The trend in maximum loading is mainly determined by the sizes of the silane molecules. The hydrophobic/hydrophilic balance of the surface functional groups mainly determines the adsorption equilibrium constants. Groups with hydrophilic functionalities, such as amines and methoxy groups, tend to have higher affinities toward the surface while less polar groups, such as alkychlorosilanes, have lower affinities toward the silica surface.

In recent years, chemists are becoming more interested in applying the mesoporous silica as host materials in adsorption[33] or nanoreactors in a chemical reaction in confined space.[3] Mesoporous silica is one of the most versatile and useful host materials for its high stability and uniformity in size and geometry. A good method of surface functionalization resulting in well-defined surface properties of the monolayer will give one complete control in the design of the nanoreactors. For example, controlled mixed grafting[34] would be achievable because we know precisely the equilibrium constants involved in grafting. This capability in surface functionalization will be very useful in future catalytic and adsorption applications.

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Supporting Information Available: N_2 absorption isotherm curves and PSDs of four silanes functionalized on HNO_3-made mesoporous silica are shown in FigureS1. The TGA plot of silylated mesoporous silica and physicochemical properties of APTS modification on FSM, MCM-41, and NMMS are also available. In addition, the loadings, equilibrium constants, Langmuir linear fittings, and the acidification process are also compared with those of other literature. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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