

# “Side Chain” Modification of MCM-41 Silica through the Exchange of the Surfactant Template with Charged Functionalized Organosiloxanes: An Efficient Route to Valuable Reconstructed MCM-41 Derivatives

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*Received: February 25, 2002; In Final Form: July 22, 2002*

The synthesis of “side chain” functionalized MCM-41 inorganic–organic hybrids, through the exchange method of the template with the cationic organosiloxanes  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ ,  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ , and  $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3^+\text{Cl}^-$  is reported. The first two derivatives are converted to free basis by neutralization of the acidic forms with  $\text{Na}_2\text{CO}_3$ . After the exchange and neutralization reactions, the as received derivatives retain the hexagonal symmetry of the original MCM-41 material, whereas, due to the high loading of the pore channels of the MCM-41 silica with the organo-modifier, the final solids exhibit rather small BET surface areas ( $\sim 100 \text{ m}^2 \text{ g}^{-1}$ ) and microporosity. The functionalized organic moieties, covalently attached to the walls of the MCM-41 mesoporous silica, exhibit the characteristic reactions of the particular end groups, including nucleophilic substitution reactions, chelation of transition metal ions, and anion exchange behavior.

## Introduction

The synergic combination of sol–gel chemistry of silicon alkoxides with the ability of surfactant molecules to form liquid crystals of a certain morphology in solution led Mobil oil company a decade ago to the discovery of a novel family of self-assembled materials denoted as M41S.<sup>1</sup> A well studied member of this family is the MCM-41 material with an hexagonal arrangement of cylindrical pores between which an amorphous silicon dioxide network is interposed.<sup>2</sup> A main drawback of these materials is their inactive chemical composition. Therefore, modification of surfaces is necessary to endow the MCM-41 materials with desirable properties, such as catalytic, environmental, or even technological. Inorganic–organic MCM-41 hybrids, a recent advance in the field, result from decorating the surfaces of the “inert” mesoporous silica with organic moieties of specific functionality (usually from an organosiloxane precursor), thus offering the possibility of utilizing these “smart materials” in various chemical and technological applications. Organically modified MCM-41 solids can be divided into three main classes, according to the location of the organic fragments in the inorganic network. In the first, the organic groups are rooted to the surfaces of the inorganic walls and protrude into the pores by (i) postsynthetic grafting of  $\text{X}-\text{Si}(\text{OR})_3$  compounds ( $-\text{X}$ : functional group) to a calcined MCM-41 silica,<sup>3,4</sup> (ii) co-condensation of a functionalized organosiloxane with the main source of the inorganic constituent, followed by acid extraction to relief the pores from the surfactant molecules,<sup>5,6</sup> and (iii) displacement of the surfactant molecules from the mesopores by an organosiloxane through interfacial reactions.<sup>7</sup> In the second class, the organic moieties are fused within the silica walls through co-condensation of organosiloxanes of the type  $(\text{RO})_3\text{Si}-\text{X}-\text{Si}(\text{OR})_3$  ( $\text{X}$ : organic spacer) with the prime silicon alkoxide, followed by extraction of the

surfactant molecules.<sup>8–12</sup> Finally, the third class comprises a combination of the aforementioned classes of inorganic–organic hybrids, e.g., other organic groups reside outside and others within the walls of the inorganic network.<sup>12</sup>

As regards the modification of the silica pores with terminal organic groups or otherwise “side chain” modification, the above methods present certain limitations. In the postsynthetic route, the small number of  $\text{Si}-\text{OH}$  groups in the calcined MCM-41 material entails a low percentage of the grafted modifier. Similarly, the co-condensation process affords materials that are, in some cases, structurally sensitive not only to the amount of the co-partner loaded onto the silica walls, but also to the surfactant extraction procedure. In addition, because the organic moieties are inhomogeneously distributed over the silica support, they are often clumped at the pore mouth of the material.<sup>12</sup> Finally, the displacement of surfactant molecules by neutral organosiloxanes is accomplished under rather intense conditions, requiring reflux of the as-synthesized MCM-41 solid in pure organosiloxane for a prolonged period of time.

The main goal of this work is to describe another efficient route for the “side chain” modification of the MCM-41 material. The method relies on simple cation exchange reactions between the electrostatically attached to the mesoporous silica surfactant cations and a positively charged organosiloxane. The method differs from the others in the following aspects: (1) the driving force causing the surfactants displacement from the MCM-41 walls is the positively charged organosiloxane species inserted into the pores, (2) the surfactant detachment and grafting of the organosiloxanes onto the surfaces of the MCM-41 material proceed simultaneously under soft conditions, (3) the method makes possible the uniform loading of the silica matrix with a high amount of modifier without destroying the organized architecture of the parent MCM-41 material, and (4) the presence of the majority of the surfactant molecules within the pore channels of the silica guarantees the same location for the most

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part of the inserted organic modifier. Nevertheless, the method is only applicable to charged organosiloxanes or amino-functionalized organosiloxanes that acquire a positive charge by protonation. The mechanism of the exchange reactions and the potentialities of such functionalized solids are also discussed.

## Synthesis

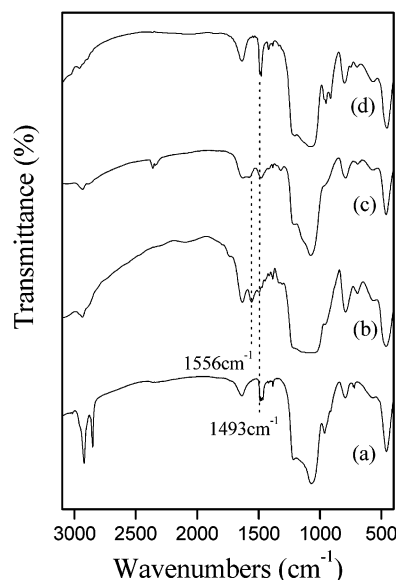
**Starting Materials.** For the synthesis of the parent MCM-41 material the following reagents were used: tetramethoxysilane (TMOS) and a 50% cetyltrimethylammonium chloride aqueous solution (C16TMACl) from Merck-Schuchardt. The following organosiloxanes were used for the MCM-41 functionalization procedures:  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ,  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ , and a 60% aqueous solution of  $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3^+\text{Cl}^-$  from Aldrich. For the silver chloride quantitative analysis, silver nitrate ( $\text{AgNO}_3$ ) from Riedel-deHaën was used.

**Procedure.** (a) *MCM-41*. The material was prepared according to a published route.<sup>13</sup> In detail, to a solution of 197.1 g of deionized water and 37.5 g of methanol was added 10.8 g of a 50% aqueous solution of C16TMACl, followed by the addition of 1.5 mL of a 50% sodium hydroxide solution. A solution of 19.5 g of TMOS in 30 g of methanol was then added to the template solution. The white precipitate, formed after a few seconds, was stirred at room temperature for 3 h. The solid was centrifuged, washed several times (5–6) with water, and then spread on a glass plate for drying.

(b) *Preparation of the Functionalized Materials*. Three samples were prepared. In a typical procedure 4 g from an as-synthesized MCM-41 material was dispersed in 100 mL of commercial ethanol containing 3 g of either  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  or  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  and an equimolar quantity of HCl. After the mixtures had been stirred for 24 h at room temperature, the solids were centrifuged, washed very well with ethanol and acetone, redispersed in a few milliliters of acetone, and finally air-dried by spreading over a glass plate. The solids were treated with a  $\text{Na}_2\text{CO}_3$  aqueous solution for 10–15 min to obtain the free bases. The products are designated as MSiAm and MSiEn for the amine and ethylenediamine based organosiloxanes, respectively. In a slightly different procedure, 4 g of the as-synthesized MCM-41 material was dispersed in 100 mL of commercial ethanol containing 4.6 g of a 60% aqueous solution of  $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3^+\text{Cl}^-$  and treated as above. After isolation and washing, the solid was dispersed in 50 mL of ethanol containing 2 drops of concentrated HCl aqueous solution (37%) and stirred for 5–10 min. The solid was centrifuged, washed well with ethanol and acetone and finally dried over a glass plate to give a product designated as MSiQAm.

All samples were additionally dried for a few hours at 80 °C in an oven before characterization.

(c) *Quantitative Silver Chloride Analysis*. To estimate quantitatively the amount of organosiloxane grafted in each functionalized solid, the chloride content of the MSiQAm and acidic forms of MSiAm and MSiEn samples were determined by quantitative silver chloride analysis. In each case, 0.5–0.6 g of modified solid was treated with 30 mL of deionized water containing 3 mL of aqueous concentrated  $\text{HNO}_3$  (65%) for 3–4 h. The solid was centrifuged, washed once with deionized water, and centrifuged again. The supernatant liquids obtained after each centrifuge process were collected and mixed together, filtered off, and placed on a conic flask wrapped with aluminum foil. To the flask was added silver nitrate, and the whole system was warmed in a water bath for ~20 min. The white precipitate



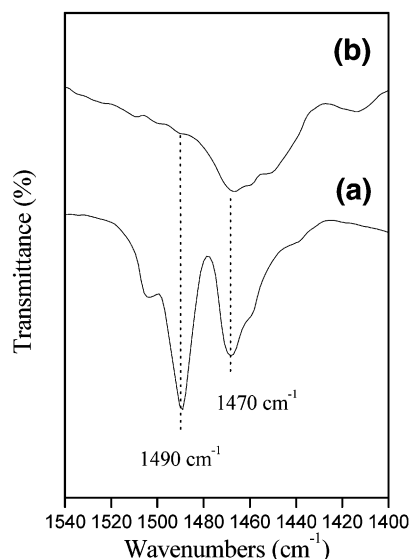
**Figure 1.** IR spectra of samples: (a) as-synthesized MCM-41, (b) MSiAm, (c) MSiEn, and (d) MSiQAm.

(silver chloride) was centrifuged, washed well with deionized water, and finally dried at 120 °C in an oven in the absence of light prior to weighing the white solid.

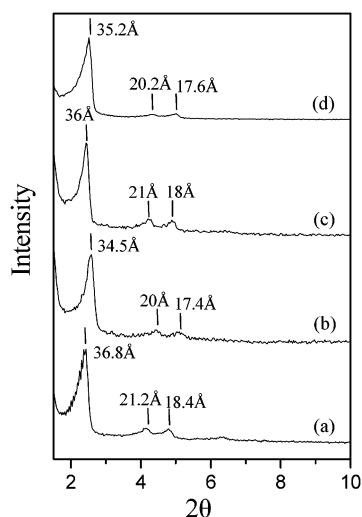
**Characterization.** X-ray powder diffraction patterns were recorded on a Siemens D-500 diffractometer using Cu K $\alpha$  radiation. The IR spectra were taken in the form of KBr pellets with a Bruker FT-IR spectrometer, Equinox 55/S model. Adsorption isotherms were taken on a nitrogen Autosorb 1 Quantacrome Corp. porosimeter at 77 K. All samples were first degassed in a vacuum at 120 °C before analysis. Electron spin resonance (ESR) measurements were carried out at 20 K on a Bruker 200D-SRC spectrometer equipped with an Oxford ESR 9 cryostat and a resonance cavity of 9.4 GHz. TEM measurements were carried out in a JEOL 120 CX microscope operating at 120 kV.

## Results and Discussion

**Characterization.** The surfactant extraction and introduction of the organosiloxane molecules to the silica surfaces in the exchange route were examined by IR spectroscopy, Figure 1. The surfactant extraction is indicated mainly by the lack of strong absorptions below 3000  $\text{cm}^{-1}$ , characterizing the surfactant aliphatic moieties, whereas the insertion of the corresponding organosiloxanes to the solid is unveiled from the presence of bands at 1556  $\text{cm}^{-1}$  ( $-\text{NH}_2$  bending vibration) for MSiAm and MSiEn derivatives, 1493  $\text{cm}^{-1}$  (broad, mainly associated with  $-\text{NH}-$  bending vibration) for MSiEn, and 1493  $\text{cm}^{-1}$  [sharp, probably arising from the  $-\text{N}(\text{CH}_3)_3^+$  moiety] for MSiQAm.<sup>14</sup> In the exchange reactions it is important to achieve total removal of the surfactant cations, because this favors the uniform distribution of the organosiloxane moieties over the silica support and also excludes clogging of the pore openings. If the pore entrances were seriously hindered by randomly located organosiloxane molecules, then total exchange of the surfactant molecules by the bulky organosiloxanes would not be expected. In addition, the complete removal of the surfactant cations ensures that the majority of the organosiloxane molecules are hosted within the pore channels of the silica network. As indicated by one of the reviewers, because both the extracted surfactant and incoming organosiloxane molecules exhibit  $-\text{CH}_2-$  groups, this makes it difficult to be conclusive about



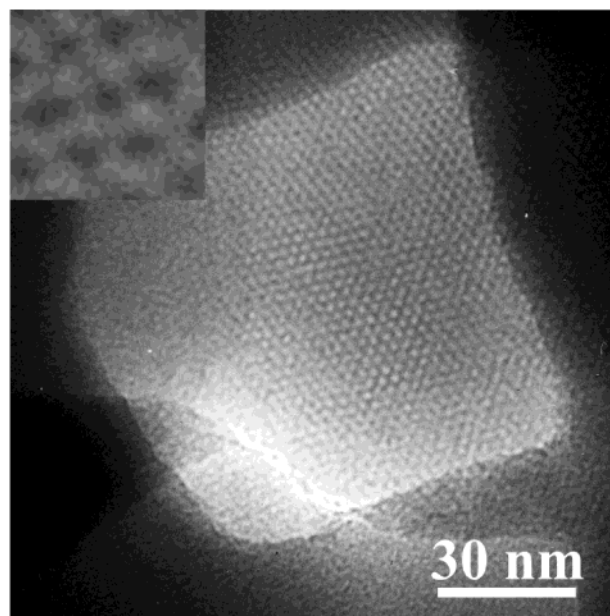
**Figure 2.** IR spectra of an MCM-41 sample prepared using cetylpyridinium bromide as the template before (a) and after (b) its treatment with  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ . The band at  $1470\text{ cm}^{-1}$  is attributed to the  $-\text{CH}_2-$  groups present in both surfactant and organosiloxane molecules.



**Figure 3.** XRD patterns of samples: (a) as-synthesized MCM-41, (b) MSiAm, (c) MSiEn, and (d) MSiQAm.

the total removal of the template based on the IR spectra. Furthermore, he points out that, in some of the cases, the neutralization process with  $\text{Na}_2\text{CO}_3$  may also contribute to the template removal. To demonstrate clearly the complete removal of the template from the silica walls during grafting of the organosiloxanes and prior to any neutralization process, we have used as the building template for the construction of the MCM-41 silica the cetylpyridinium bromide surfactant. The IR spectra, presented in a selected region, of the as-made MCM-41 solid before and after its treatment with, for instance,  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ , are shown in Figure 2. Accordingly, we discern that the sharp, characteristic band at  $1490\text{ cm}^{-1}$ , due to vibrations of the pyridinium group, disappears completely after treatment with the protonated organosiloxane, thus giving strong evidence for total removal of the template after the exchange reactions and prior the neutralization process.

Figure 3 presents the XRD patterns of a pure MCM-41 sample and of the organically modified MSiAm, MSiEn, and MSiQAm derivatives. It is seen that the functionalized materials retain the typical hexagonal symmetry for an MCM-41 solid through-



**Figure 4.** TEM micrograph for the MSiQAm solid.

out the entire synthesis. In addition, the extraction of the surfactant molecules and the covalent grafting of the corresponding organosiloxanes to the silica walls do not induce considerable lattice shrinkage, as indicated by the similar  $d_{100}$  values. These results suggest that upon replacement of the surfactant cations by the positively charged organosiloxanes the MCM-41 architecture remains intact. Accordingly, it is safe to assume that the organosiloxane units act as effective scaffolders in stabilizing the mesoporous silica walls. In contrast to the exchange route, when the co-condensation and surfactant extraction procedures were tested for the modification of the silica pores with an amine or quaternary amine functionalized organosiloxanes, problems were encountered. More specifically, the addition to the initial solution in the synthesis of the MCM-41 material of a small quantity of organosiloxane (TMOS/Modifier molar ratio: 9/1, total molar silicon: constant), although led to crystalline materials for the  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  and  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  modifiers, it afforded an almost amorphous product for the case of  $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ . More importantly, we found that, unlike other reports,<sup>15</sup> the acid extraction of the surfactant from the amine and ethylenediamine based functionalized solids gave products with a totally collapsed structure.

Figure 4 shows a TEM micrograph for the MSiQAm sample. The image discloses that the silica particles retain the characteristic regular hexagonal pore arrangement of the MCM-41 material, exhibiting uniform structural features and unblocked pore channels. The lattice parameter  $a_0$  is estimated to be  $\sim 39\text{ Å}$ , a value very close to that estimated from the XRD pattern of the corresponding sample ( $42.5\text{ Å}$ ,  $a_0 = 2/\sqrt{3}d_{100}$ ), whereas the pore diameter and wall thickness are  $20$  and  $19\text{ Å}$ , respectively. Similar pictures were obtained for the MSiAm and MSiEn samples. Note that no degradation of the organic matter was observed at  $120\text{ kV}$  during the TEM study.

At this point, we must emphasize that due to the efficient coverage of the pores with significant amounts of terminal, bulky organosiloxane units (vide infra), a large part of the pore space is occupied by the organic fragments. As a result, the functionalized samples are expected to exhibit, and indeed exhibit, small BET surface areas ( $\sim 100\text{ m}^2\text{ g}^{-1}$ ). It is also worth noticing that the adsorption-desorption isotherms are quite reminiscent of microporous materials, as shown for sample MSiQAm in Figure



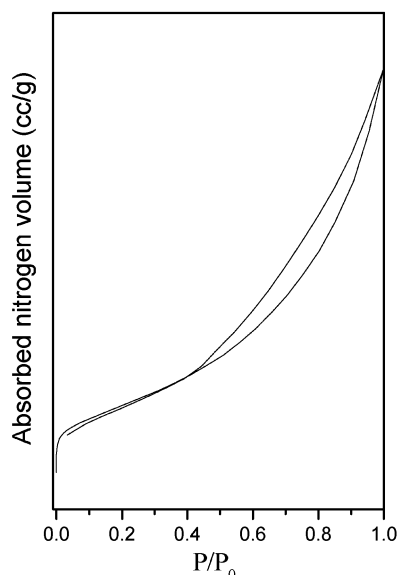


Figure 5. Adsorption-desorption isotherms for the MSiQAm sample.

5. This means that, the effective pore diameter of each sample is smaller than the value estimated from TEM results. A rough estimation, based on the length of the organic fractions of the organosiloxanes and assuming the formation of a monolayer over the silica surfaces, gives a pore diameter of about 10 Å. A more accurate value can be determined with the Horvath-Kawazoe model, which permits to calculate the pore size distribution in the microporous region. Accordingly, a mean pore diameter of 7–8 Å was found for all samples.

The present exchange route enables feeding of the mesoporous silica with a considerable amount of organosiloxane. This was verified by performing silver chloride quantitative analysis for the MSiQAm and the acidic forms of the MSiAm and MSiEn derivatives, to determine the anion exchange capacity (AEC) in the chloride form of each solid. The MSiAm·HCl solid exhibited an AEC of 2.5 mequiv g<sup>-1</sup>, the MSiEn·HCl of 1.7 mequiv g<sup>-1</sup>, and the MSiQAm of 1.4 mequiv g<sup>-1</sup>, values that are significantly higher than those found for the post-grafted analogues. Particularly, in blank experiments using a calcined MCM-41 sample in place of an as-synthesized sample and analyzing quantitatively the solids obtained from the post-grafting procedure, we found the following AEC values: 0.8 mequiv g<sup>-1</sup> for MCSiAm·HCl, 0.65 mequiv g<sup>-1</sup> for MCSiEn·HCl, and 0.45 mequiv g<sup>-1</sup> for MCSiQAm, where the extra label C denotes the calcined state of the MCM-41 silica. Apparently, the lower AEC values found for the post-grafted samples arise from the small number of Si–OH units in the calcined MCM-41 material. As far as the AEC ordering is concerned, this is the same for both series of functionalized solids (as-synthesized and calcined) and can be attributed to the different size of each inserted species. For instance, the size of the amine based organosiloxane (methoxy form) is smaller than the ethylenediamine analogue (methoxy form) and therefore grafting of the former to the silica surfaces meets smaller steric hindrance from neighboring molecules. The quaternary ammonium type organosiloxane (ethoxy form) is expected to show a smaller reactivity not only because of its size but also because of its smaller rate of condensation toward the Si–OH groups owing to the ethoxy groups of the organosiloxane.

**Mechanistic Consideration.** The exchange method of the template is a well established route that has been successfully applied mostly for imbibing to the walls of the MCM-41

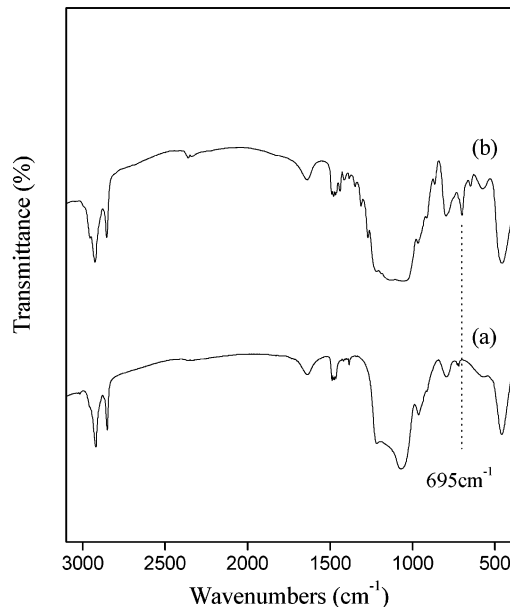


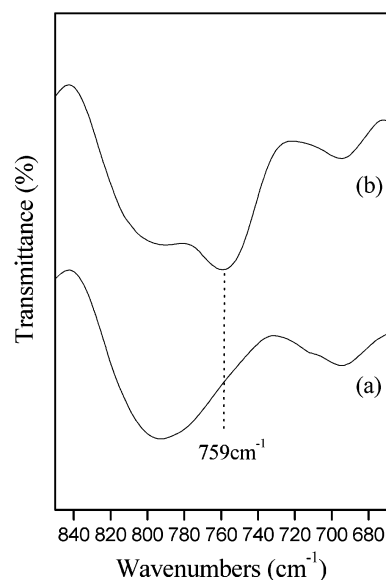
Figure 6. IR spectra of an as-synthesized MCM-41 sample before (a) and after (b) its treatment with (CH<sub>3</sub>O)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl.

material metal ions, semiconductors, magnetic oxides, or metal complex species.<sup>16–21</sup> The method simply relies on cation exchange reactions between the positively charged surfactant molecules and metal cations, metal oligonuclear cations, or metal complex cations that are grafted to the silica surfaces via the Si–O<sup>-</sup> sites of the parent MCM-41 solid in a specific mode of coordination. Recently, we have emphasized that the connectivity of the silica network has a significant effect on the structural integrity of a modified MCM-41 material after an exchange procedure.<sup>20</sup> The presence of a large number of noncondensed silanol groups in an as-synthesized MCM-41 solid weakens the silica walls, and upon total removal of the surfactant molecules, the latter acting as pillars in the MCM-41 framework, products of poor crystallinity result. Therefore, drying at 100 °C for a prolonged period of time was necessary prior to the exchange procedure to promote the condensation reactions among the free silanol groups in the solid and strengthen the inorganic network. The same exchange principles hold also in the present case. First of all, the driving force leading to the displacement of the surfactant molecules is the cationic nature of the robust organosiloxane species. A blank experiment with (CH<sub>3</sub>O)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl showed that surfactant displacement did not take place upon treating the as-synthesized MCM-41 solid with the organosiloxane, except a probable grafting at the external surfaces through condensation with existing free silanol groups.<sup>22</sup> The IR spectra, Figure 6, show the surfactant characteristic absorption bands below 3000 cm<sup>-1</sup> (intact in intensity) and also a new band at 695 cm<sup>-1</sup> attributed to the C–Cl stretching vibration in the organo-modifier.<sup>14</sup> Similarly, blank experiments with the neutral (CH<sub>3</sub>O)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> and (CH<sub>3</sub>O)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> derivatives did not affect the state of the surfactant molecules in the as-synthesized MCM-41 solid. Second, once the organosiloxane cations have penetrated the pore channels of the silica matrix, they are linked to surfaces through condensation and formation of covalent Si–O–Si bonds and not through electrostatic or hydrogen bonding interactions between the organosiloxane and silica surfaces, e.g. (RO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>O<sup>-</sup>–Si or (RO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>X···HO–Si, where X = –NH<sub>2</sub>, –NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, R = –CH<sub>3</sub>, –CH<sub>2</sub>CH<sub>3</sub>. For instance, treatment of MSiQAm with C16TMACl in aqueous solution does not restore the surfactant presence in the

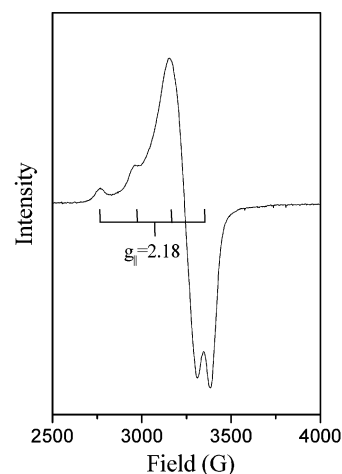
solid, whereas treatment of the MSiAm and MSiEn with ethanol does not extract the inserted organo-modifiers. Finally, there is no need to dry the as-synthesized MCM-41 material prior to the exchange reactions, because, according to the XRD results, the grafted organosiloxane molecules act as scaffolders and prevent the collapse of the MCM-41 construction after displacement of the surfactant molecules.

As described in the Experimental Section, the synthesis of the MSiQAm derivative comprises an additional treatment with a dilute HCl ethanol solution. This treatment proved to be crucial for the stability of the MSiQAm product, especially against water, and also for its total anion exchange capacity. When this step was omitted, the received product had a lower AEC (0.9 mequiv  $\text{g}^{-1}$  versus 1.4 mequiv  $\text{g}^{-1}$  for the acid treated sample) and, furthermore, upon dispersion in water for a few hours, it lost a significant part of its anion exchange capacity (0.5 mequiv  $\text{g}^{-1}$ ). Likewise, the same conclusion was reached by IR spectroscopy from the considerable decrease in the intensity of the sharp band at  $1493\text{ cm}^{-1}$  after water treatment. A possible explanation for this behavior rests on the fact that, during the exchange procedure the condensation reactions between the ethoxy groups of the quaternary ammonium type organosiloxane and the  $\text{Si}-\text{O}^-$  units of the silica support, liberate a considerable amount of ethoxy anions ( $\text{C}_2\text{H}_5\text{O}^-$ , strong base) that due to the water are hydrolyzed instantly to give  $\text{OH}^-$  anions. It is reasonable to assume that these hydroxy anions antagonize the chloride ions as balancing ions in the hybrid structure and lower its chloride type AEC (notice that the  $\text{OH}^-$  anions do not "contribute" to the measured AEC value because they are neutralized by the  $\text{HNO}_3$  used for the extraction of the chloride ions from the hybrid solid). Furthermore, the particular solid is sensitive against water owing to the potential alkaline hydrolysis of the  $\text{Si}-\text{O}-\text{Si}$  bonds that bridge the organo-modifier with the silica surfaces. Accordingly, the addition of HCl neutralizes the hydroxy ions, restores the total AEC of the solid in the chloride form, and guarantees the necessary stability against water. Indeed, the dispersion of an acid treated MSiQAm sample in water for 24 h did not affect seriously the bonded organosiloxane moieties and thus the AEC of the hybrid solid. Noticeable, because in a calcined MCM-41 sample there are present only  $\text{Si}-\text{OH}$  and not  $\text{Si}-\text{O}^-$  groups, the problems from the generation of the  $\text{OH}^-$  anions during grafting of the quaternary type organosiloxane cations to the silica surfaces are not encountered. On the other hand, in the MSiAm and MSiEn cases the liberated  $\text{OH}^-$  anions are effectively neutralized by the excess of protonated amines of the organosiloxane molecules present in the bulk liquid, thus making unnecessary the acid treatment step.

**Potentialities of the Functionalized Materials.** Owing to the organosiloxane functional end groups [ $-\text{NH}_2$ ,  $-\text{NHCH}_2\text{CH}_2\text{NH}_2$ , and  $-\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ ] the inorganic-organic hybrid MCM-41 materials inherit all the characteristic and desirable properties of these groups, such as nucleophilic substitution (MSiAm), sequestering of transition metal ions (MSiEn), and anion exchange properties (MSiQAm). The following tests demonstrate these concepts: (i) a sample of MSiAm was allowed to react with salicylic aldehyde in alcohol to give instantly the corresponding yellow Schiff base product, (ii) an aqueous dispersion of MSiEn when treated with an aqueous  $\text{Cu}^{2+}$  solution gave a blue product indicative of copper chelation by the ethylenediamine end groups of the particular modifier and (iii) solid  $\text{MSiQAm}^+\text{Cl}^-$  was simply exchanged with  $\text{Fe}(\text{CN})_6^{4-}$  anions in aqueous solutions to afford the ferrocyanide analogue. Notice that all samples retained their hexagonal



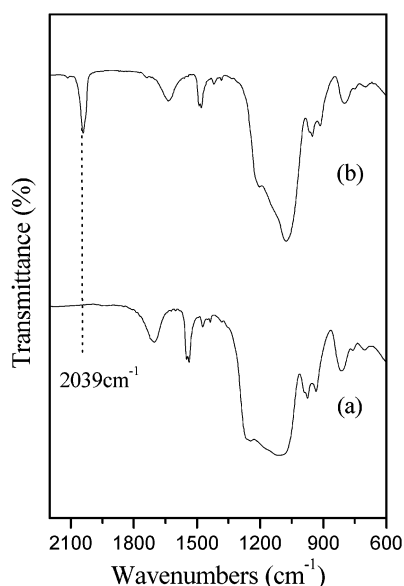
**Figure 7.** IR spectra of MSiAm before (a) and after (b) reaction with salicylic aldehyde.



**Figure 8.** ESR spectrum at 20 K of MSiEn after treatment with copper ions.

symmetry after each modification, as evidenced by XRD measurements.

Figure 7 presents the IR spectra of MSiAm before (a) and after (b) modification with salicylic aldehyde (reaction time 2 h). Spectrum b exhibits an absorption band at  $759\text{ cm}^{-1}$  that does not exist in spectrum a. This band, arising from the four adjacent hydrogens in the aromatic ring, indicates attachment of the salicylaldehyde molecules.<sup>14</sup> It should, however, be pointed out that complete reaction with the amine groups in the solid was not successful even after a prolonged reaction time ( $\sim 1$  week). This can be ascribed to a gradually slower diffusion of the salicylaldehyde molecules into the pores because of their partial obstruction by the already generated bulky imine derivative.<sup>6</sup> Figure 8 depicts the ESR spectrum of the MSiEn solid after its treatment with copper ions, recorded at 20 K. The spectrum of the frozen solid can be described by an axial spin Hamiltonian with parameters  $g_{\parallel} = 2.18$ ,  $g_{\perp} = 2.07$ , and  $A_{\parallel} = 0.0182\text{ cm}^{-1}$ , which point to copper ions coordinated to four nitrogens in a square planar symmetry.<sup>23,24</sup> The fact that two chelating moieties can bind one copper ion signal for a dense packing of the organosiloxane moieties onto the surfaces of the silica support. Finally, the exchange of the chloride ions of the MSiQAm material (AEC: 1.4 mequiv  $\text{g}^{-1}$ ) by the ferrocyanide



**Figure 9.** IR spectra of MSiQAm before (a) and after (b) exchange with  $\text{Fe}(\text{CN})_6^{4-}$  ions.

anions is easily established by IR spectroscopy, Figure 9. It is clear that after exchange, the received solid exhibits a strong absorption band at  $2039\text{ cm}^{-1}$  arising from the vibrations of cyanide ligands. This observation has particular interest, because in an envisioned application, feeding the pore channels with anionic metal complexes  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $[\text{PtCl}_6]^{2-}$ , followed by calcination of the issuing derivatives could lead to metal oxides ( $\alpha\text{-Fe}_2\text{O}_3$ , magnetic  $\gamma\text{-Fe}_2\text{O}_3$ ) or metallic (Pt)<sup>25</sup> nanoparticles embedded within the pore channels of the MCM-41 siliceous support.

## Conclusions

In the present work we have described an efficient and simple route for the synthesis of "side chain" inorganic–organic MCM-41 hybrids. The method is based on cation exchange reactions between the surfactant molecules of an as-synthesized MCM-41 material and positively charged functionalized organosiloxane compounds. The method enables a uniform feed of the mesoporous silica walls with sufficient amounts of organo-modifiers without destroying the typical hexagonal arrangement of

cylindrical pores for an MCM-41 material. The hybrid solids inherit the attractive properties of the functional end groups of the attached organosiloxanes, thus making feasible further modifications of the solids to novel and valuable reconstructed MCM-41 derivatives.

## References and Notes

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