# *Articles*

# Comparative Study of Silylation Methods to Improve the Stability of Silicate MCM-41 in Aqueous Solutions

Jenny M. Kisler,[†] Michelle L. Gee,[‡] Geoffrey W. Stevens,[†] and
Andrea J. O'Connor*,[†]

*Department of Chemical Engineering and School of Chemistry, The University of Melbourne,
Victoria 3010, Australia*

The stability of silicate MCM-41 in aqueous solutions for up to 12 days has been dramatically improved by silylation with hexamethyldisilazane (HMDS). Mesoporous molecular sieves including MCM-41 show promise for application as selective media for separations of large molecules such as proteins, which are important in the food and pharmaceutical industries. However, many such applications involve aqueous solutions in which MCM-41 has limited stability. Thus, hexamethyldisilazane has been used to create a hydrophobic surface coating on both flat silica and MCM-41 in order to improve their stability in aqueous solutions. This coating was shown to persist on the flat surfaces after aging in water for up to 7 days, using contact angle measurements and atomic force microscopy, unlike a coating applied using trichloromethylsilane which was removed by water. The HMDS-coated MCM-41 showed much greater structural stability than uncoated MCM-41 in both water and an aqueous potassium phosphate buffer solution of pH 6 for extended periods.

## Introduction

Molecular sieves are widely used in industry for the separation of small molecules from mixtures. The discovery of the highly ordered M41S mesoporous silicate materials has extended the size range available for these separations which was previously limited to zeolites with pores of less than 1.5 nm. Silicate and aluminosilicate materials have been synthesized with specific surface areas of approximately 1000 $m^2 \cdot g^{-1}$ and uniform pore sizes which can be adjusted in the 1.5–10 nm range. One member of this family, MCM-41, is recognized as having a hexagonal array of uniform pores.[1]

The advantages of ordered silicate mesoporous materials for separation applications include a regular array of uniform pores, controllable pore size, and the ability to functionalize the surface for particular separations. Furthermore, MCM-41 has a rigid structure and so avoids the swelling problems encountered with some other adsorbents. Potential separation applications for MCM-41 include protein separation[2,3] and mercury removal from waste streams.[4,5]

However, the stability of these materials in aqueous solutions is of concern. Although the properties of M41S

materials have been widely investigated, only limited studies have been performed after their exposure to aqueous solutions. Most of these studies have focused on the hydrothermal stability of the materials by assessing their structure before and after treatment in boiling water for up to 48 h.[6,7] However, it is important that the pore structure integrity is retained throughout repeated adsorption and regeneration cycles, generally performed around room temperature, if these materials are to be economically employed in separation processes involving aqueous solutions. Recent work has shown that the M41S materials are modified by prolonged exposure to water and water vapor, showing decreased structural regularity, pore shape uniformity, pore size, and pore volume.[7–11] On solution contact, basic solutions in particular cause major loss of structure with much larger pores and decreased surface areas found in

---

* To whom correspondence should be addressed. Tel: +61 3 8344 8962. Fax: +61 3 8344 4153. E-mail: andreajo@unimelb.edu.au.
† Department of Chemical Engineering.
‡ School of Chemistry.

(1) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992,** *114,* 10834.
(2) Kisler, J.; Daehler, A.; Stevens, G. W.; O'Connor, A. J. *Micropor. Mesopor. Mater.* **2001,** *44–45,* 769.
(3) Han, J.; Stucky, G. D.; Butler, A. *J. Am. Chem. Soc.* **1999,** *121,* 9897.
(4) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997,** *9,* 500.
(5) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997,** *276,* 923.
(6) Lim, M. H.; Stein, A. *Chem. Mater.* **1999,** *11,* 3285.
(7) Yamamoto, K.; Tatsumi, T. *Micropor. Mesopor. Mater.* **2001,** *44–45,* 459.
(8) Ribeiro Carrott, M. M. L.; Estevao Candeias, A. J.; Carrott, P. J. M.; Unger, K. K. *Langmuir* **1999,** *15,* 8895.
(9) Zhao, X. S.; Audsley, F.; Lu, G. Q. *J. Phys. Chem. B* **1998,** *102,* 4143.
(10) Igarashi, N.; Tanaka, Y.; Nakata, S.; Tatsumi, T. *Chem. Lett.* **1999,** *1,* 1.
(11) Van der Voort, P.; Mathieu, M.; Vansant, E. F. *Stud. Surf. Sci. Catal.* **2001,** *135,* 06-P-06.

materials immersed for short periods, e.g., several hours.[12,13] Little change was observed in the properties for materials exposed to neutral or acidic solutions over periods up to 48 h.[12,13] Water immersion was found to have greater impact on the structure as the temperature of the solution was increased in the range 298−373 K.[14] This low stability restricts the life of M41S materials in aqueous solutions, and has, to date, limited the range of applications for these materials.

Variations on the synthesis methods, such as adjustment of pH or addition of salt, or postsynthesis treatments have been shown to improve the stability of M41S materials.[8,11,12,15,16] The relatively low wall thickness of these materials contributes to their lack of stability, so thicker-walled materials also show improved stability.[11,16] Modification of mesoporous silicates to include hydrophobic organic components on the pore surfaces or within the walls, either by co-condensation or postsynthesis grafting, has been found to improve their stability in the presence of water.[9,16,17] This has also been shown to improve the materials' structural stability and thereby their mechanical stability under compression.[10,11,17] Lim and Stein demonstrated that a vinyl-functionalized MCM-41 sample prepared by postsynthesis grafting had greater hydrothermal stability than untreated MCM-41 when placed in boiling water for 24 h.[6] However, the functionalized sample was still noticeably degraded in this time with a significant broadening of the pore size distribution in the range of 3−8 nm and a 49% increase in the pore volume. Application of MCM-41 in separation processes involving solution contact will require significantly longer term stability than has been exhibited by these modified samples to date, with minimal changes to the porous structure.

Organic modification of the surfaces of M41S materials appears to be a promising route for structural stabilization as well as providing control over the surface chemistry of the materials, which may be used to enhance their separation selectivity. However, studies performed on flat silica surfaces have shown that not all hydrophobic coatings generally used on silica form covalently bound layers, and that the quality of silylation coatings can be critically dependent on the level of surface water on the silica, a factor which is difficult to control.[18,19] In particular, the commonly used alkyltrichlorosilanes do not react with silica surfaces in the absence of water below 300 °C. Tripp and Hair have demonstrated, by using infrared spectroscopy, that treatment of hydrated silica at room temperature with trichloromethylsilane (TCMS) results in the formation of methyltrisilanol which partially cross-links but does not condense with the silica surface.[19,20] Therefore, the alkyltrichlorosilanes tend to form physically adsorbed

layers on the silica surface with hydrogen bonding to the surface hydroxyls rather than reacting to form covalent bonds. It is possible, however, to achieve a chemically attached coating with TCMS at room temperature by employing a two-step reaction using an amine to promote the reaction of the silane with the surface.[21] Grignard reagents have also recently been investigated to produce a robust grafted coating on mesoporous silicates,[7,22] but these too require more difficult procedures due to the reactivity of the reagents with water.

Hexamethyldisilazane (HMDS) was chosen as a silylating agent to improve the stability of MCM-41 in this work, as the formation of siloxane bonds from the reaction between gaseous HMDS and the surface hydroxyl groups of flat silica surfaces has been demonstrated using infrared spectroscopy.[23] Several different disilazanes have been investigated for reaction with MCM-41, with a surface coverage of 0.74 to 1.85 silyl groups·nm$^{-2}$ found depending upon the disilazane used.[24] These silylating agents were found to be very effective for the modification of mesoporous materials due to their relatively slow, monofunctional surface reaction and ease of desorption of the ammonia byproduct. However, the stability of these coatings in aqueous solution has not been previously reported. In this report, we compare the durability in water of coatings formed on flat silica plates with HMDS and the two-step amine promoted reaction with TCMS. We then report on the dramatic improvements to the structural stability of MCM-41 upon extended exposure to aqueous solutions after silylation with HMDS.

## Experimental Section

Si-MCM-41 materials were synthesized using standard hydrothermal synthesis and calcination methods.[1,25,26] These materials were characterized using X-ray powder diffraction (XRD) (Philips PW1800 diffractometer, Cu Kα radiation of wavelength 1.54056 Å) and gas adsorption analysis (Micromeritics ASAP 2000 using nitrogen at 77 K). The gas adsorption data were used to calculate surface areas from the BET model,[27] as well as average pore diameters and pore size distributions from the adsorption branch of the isotherm using the BJH model.[28,29] Total pore volumes were estimated based on the amount of nitrogen adsorbed at a relative pressure of about 0.99.[30]

A hydrophobic surface coating was applied to two batches of calcined MCM-41 (designated as samples A and B) following characterization. Initially a vacuum was applied to the vessel containing the MCM-41 powder. The silylating agent, hexamethyldisilazane (HMDS, Merck 98%), was degassed by a series of freeze−thaws under vacuum in an adjacent vessel, isolated from the MCM-41 by a valve, and was then allowed

(12) Landau, M. V.; Varkey, S. P.; Herskowitz, M.; Regev, O.; Pevzner, S.; Sen, T.; Luz, Z. *Micropor. Mesopor. Mater.* **1999**, *33*, 149.

(13) Trong On, D., Zaidi, S. M. J.; Kaliaguine, S. *Micropor. Mesopor. Mater.* **1998**, *22*, 211.

(14) Ryoo, R.; Jun, S. *J. Phys. Chem. B* **1997**, *101*, 317.

(15) Edler, K. J.; White, J. W. *J. Mater. Chem.* **1999**, *9*, 2611.

(16) Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, *12*, 1403.

(17) Koyano, K., Tatsumi, T, Tanaka, Y, Nakata, S. *J. Phys. Chem. B* **1997**, *101*, 9436.

(18) Hair, M. L.; Tripp, C. P. *Colloids Surf. A: Physicochem. Eng. Aspects* **1995**, *105*, 95.

(19) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 149.

(20) Tripp, C. P.; Hair, M. L. *Langmuir* **1992**, *8*, 1961.

(21) Tripp, C. P.; Hair, M. L. *J. Phys. Chem.* **1993**, *97*, 5693.

(22) Kang, K.-K.; Rhee, H.-K. *Stud. Surf. Sci. Catal.* **2001**, *135*, 29-P-09.

(23) Hertl, W.; Hair, M. L. *J. Phys. Chem.* **1971**, *75*, 2181.

(24) Anwander, R.; Nagl, I.; Widenmeyer, M.; Engelhardt, G.; Groeger, O.; Palm, C.; Roser, T. *J. Phys. Chem. B* **2000**, *104*, 3532.

(25) Zhao, X. S.; Lu, G. Q.; Whittaker, A. K.; Millar, G. J.; Zhu, H. Y. *J. Phys. Chem. B* **1997**, *101*, 6525.

(26) Zhao, X. S.; Lu, G. Q. *J. Phys. Chem. B* **1998**, *102*, 1556.

(27) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(28) Branton, P. J.; Sing, K. S. W.; White, J. W. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2337.

(29) Kruk, M.; Jaroniec, M.; Sayari, A. *Langmuir* **1997**, *13*, 6267.

(30) Kruk, M.; Jaroniec, M.; Kim, J. M.; Ryoo, R. *Langmuir* **1999**, *15*, 5279.

to thaw. Following the freeze−thaw process, the vessel containing the MCM-41 was heated. The temperature was gradually increased over several hours until a temperature of 300 °C was reached. The sample was maintained at this temperature and under vacuum for at least a further 8 h so that all water physisorbed in the pores of the MCM-41 was removed. The heater was then turned off and the vessel was isolated from the vacuum line. The valve to the silylating agent reservoir was opened and the HMDS vapor and MCM-41 powder were allowed to react. The chamber was left to cool to room temperature as the reaction occurred. The materials were allowed to react overnight (minimum 16 h). After cooling the vessel was opened and the powder was recovered. This coated material was then stored in a desiccator.

Stability tests on coated and uncoated MCM-41 from sample B were conducted. This involved the contact of 350 mg of MCM-41 with 250 mL of solution, being either distilled water or a pH 6 potassium phosphate buffer (50 mM). These tests were conducted at room temperature (298 K) with slow stirring.

Silica microscope slides (Livingstine; cut to $10 \times 10$ mm squares) were used as flat surfaces for characterization of the coatings applied to the silica surfaces by methods not feasible on the mesoporous samples. Before coating, the slides were cleaned in an aqueous solution of 50% hydrogen peroxide containing five drops of ammonia. The slides were heated to 60 °C in this solution and retained at this temperature until fine bubbles were featured all over the surface, and then rinsed with water.

The flat silica surfaces were coated with HMDS or TCMS (99%, Aldrich). HMDS was coated onto the flat silica plates following the same procedure used for the coating of MCM-41, as described above. The only exception was that the plates were retained at temperature for only 2 h prior to reaction. The TCMS coating was formed using a method previously described which involves an initial reaction with an amine followed by reaction with the chlorosilane.[21] The amine used was triethylamine (TEA, Ajax Finechem). Bulbs of TEA and TCMS were attached to, and isolated from, the vacuum line, which was attached to the reaction vessel. Liquid nitrogen was used to freeze/thaw the reagents. The silica slides were heated to 200 °C under vacuum to remove physisorbed water. The vacuum pump was then isolated from the plates which were then exposed to TEA vapor for 20 min. Any excess reagent was then removed by vacuum after reaction. The plates treated with the TEA were then exposed to TCMS vapor for over an hour with the excess again removed by vacuum.

The flat silica surfaces were aged by placing them into water purified using a Milli-Q water purification system (conductivity $<10^{-6}$ S·cm$^{-1}$), with the exception of one slide which was studied without solution contact. These surfaces were removed from the water after varying time periods and dried in a desiccator overnight. The effects of aging on the surface coatings of the plates were studied by AFM imaging to monitor surface topography. The wetability of the sufaces was monitored concurrently by contact angle measurement. Contact angles were measured using the sessile drop technique. The instrument employed for this was a contact angle system OCA (Dataphysics). Atomic force microscopy (AFM) images were taken with a Nanoscope III AFM (Digital Instruments) and were recorded with the AFM-J piezoelectric scanner which has a lateral scan area of up to $140 \times 140$ $\mu$m. The cantilever tips used have a manufacturer's spring constant of 0.12 N·m$^{-1}$. The J scanner was calibrated prior to imaging with an optical diffraction grating and a compact disk stamper of known lateral and vertical dimensions, respectively. Images were recorded in the constant force mode, under ambient conditions in air with a scan rate of around 2 Hz.

## Results and Discussion

The advancing contact angle of water was measured for both TCMS and HMDS treated silica plates. To test the stability of these coatings, the measurements were taken on plates dried after varying times of exposure

**Table 1. Summary of Contact Angle and AFM Measurements for Uncoated and Coated Flat Silica Surfaces**

| silylating agent | aging period in water (hr) | RMS roughness (nm) from AFM images | contact angle with water (deg) |
|---|---|---|---|
| clean surface | 0 | 0.45 | 0 |
| HMDS | 0 | 13.3 | 69 |
| HMDS | 17 | 0.8 | 56 |
| HMDS | 45 | 0.7 | 58 |
| HMDS | 70 | 0.8 | 45 |
| HMDS | 143 | 0.6 | 52 |
| HMDS | 168 | 0.6 | 47 |
| TCMS | 0 | 3.0 | 70 |
| TCMS | 48 | 0.5 | 20 |
| TCMS | 200 | | <3 |
| TCMS | 384 | 0.45 | |

to water, as described above in the Experimental section. The results obtained are shown in Table 1. It should be noted at the outset that a clean, uncoated silica surface is perfectly wetting, such that the contact angle of water on a fully hydroxylated silica surface is zero. The contact angle measured immediately after reaction with either HMDS or TCMS increases dramatically to 69° in the case of the HMDS coating, and to 70° for the TCMS coating. This indicates that a hydrophobic layer is formed on silica after exposure to either silylating agent.

However, of importance in the application of mesoporous silicates to aqueous-based processes such as adsorption of biological molecules, is the robustness of these hydrophobic layers when exposed to water. The contact angle of water on coated plates after aging in water indicates that the TCMS layer is not at all stable. After only 48 h of exposure to water, the contact angle decreases dramatically from its initial value of 70° to only 20°. This implies that the TCMS layer has undergone significant degradation. Indeed, after 200 h of aging in water, the silica surface has become hydrophilic again, as it was prior to silylation, with a contact angle less than 3°. Clearly, water is able to displace the TCMS layer relatively easily, thus revealing a fully hydroxylated silica surface. This result demonstrates that the TCMS did not chemically react with the silanol groups at the silica surface, despite the use of the two step reaction. Rather, it formed a physisorbed layer on the silica. Our results confirm this by showing that the layer is easily displaced by water. If TCMS were chemically anchored at the surface, it would be much more difficult to remove. This would seem to indicate that the two-step reaction is sensitive to reaction conditions and may not achieve a chemically bound coating if the conditions are not perfect.

In contrast, HMDS appears to form a relatively robust surface layer on silica quite easily. The initial contact angle is 69° and drops only a small amount to 56° when exposed to water for 17 h. Prolonged water exposure leads to a further drop in contact angle of only 9°, approximately. Note that there is some inaccuracy in any sessile drop contact angle measurement of around ±5° due to surface heterogeneity and drop evaporation which is difficult to control.

AFM images of coated silica plates after water exposure corroborate the contact angle measurements and the above discussion. A series of AFM images of both TCMS and HMDS coated silica plates are pre-
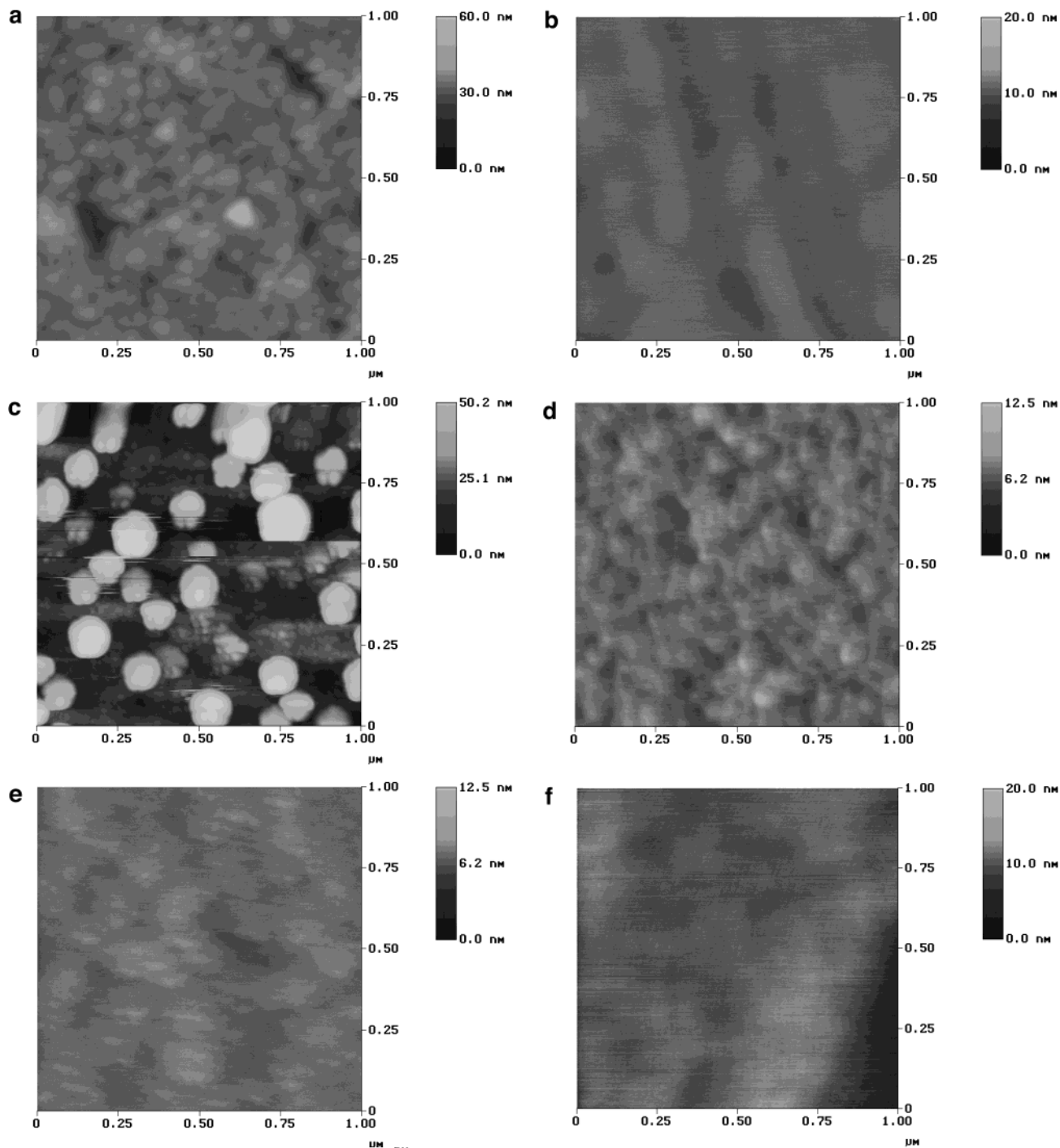
**Figure 1.** AFM images of silica plates before and after aging in water:  (a) TCMS-coated plate immediately after reaction; (b) TCMS-coated plate after 384 h in water; (c) HMDS-coated plate immediately after reaction; (d) HMDS-coated plate after 17 h in water; (e) HMDS-coated plate after 143 h in water; and (f) uncoated silica surface.

sented in Figure 1a−e. Also presented is an AFM scan of a clean, uncoated silica surface for comparison (Figure 1f). AFM imaging also yields an RMS surface roughness. These numbers are given in Table 1.

Figure 1a clearly indicates the presence of a relatively rough surface layer of TCMS that appears in the image as roundish lumps. The RMS roughness of bare silica is 0.45 nm and increases to 3.0 nm after coating with TCMS. These lumps are not present on the bare silica surface (Figure 1f). However, after 48 h of exposure to water (image not shown), these lumps are no longer present and the TCMS layer has a sparse, matted appearance with an RMS roughness of 0.5 nm, similar

to that for the bare silica surface (i.e., 0.45 nm). It appears that the originally lumpy TCMS coating is dissolving away from the surface as a result of water exposure. The contact angle of 20° on this surface, as discussed above, confirms that the TCMS layer is indeed degrading. Figure 1b is an AFM image of a TCMS treated silica plate after 384 h exposure to water. There is very little to distinguish this figure from that of a clean, untreated silica plate, as can be seen by comparing Figure 1b and f. Indeed, the RMS roughness is the same as that for clean, untreated silica and the contact angle after 200 h of exposure to water is <3°. Water has displaced the TCMS layer indicating that it is only

physisorbed, confirming the conclusions made from the contact angle measurements.

Figure 1c is an AFM image of a silica surface immediately after treatment with HMDS. Note that the surface is covered with a large number of individual lumps and is extremely rough with an RMS roughness of 13.3 nm, much greater than that for the fresh TCMS layer (i.e., 3.0 nm). Exposure of silica to HMDS has clearly led to the formation of some sort of surface coating and this coating is hydrophobic, as discussed above. After 17 h of exposure to water, the large lumps initially present on the silica surface are completely gone (see Figure 1d) and the RMS roughness has decreased dramatically to only 0.8 nm. There still appears to be some sort of layer, as the image is different from that for bare silica (Figure 1f). Interestingly, although the images of the surface layer appear very different, there is only a relatively small decrease in contact angle from 69° immediately after coating to 56° after 17 h of water exposure. It seems that there is a smooth, hydrophobic HMDS layer underneath the lumps that were originally present on the surface. Given the ease with which these lumps were displaced it can be concluded that they were some unreacted material or reaction byproduct that was only loosely adsorbed onto the HMDS layer. After continued aging of the HMDS-coated silica plates for 143 or 168 h, the appearance of the surface layer did not markedly change (compare Figure 1d and e). There is only a slight decrease in surface roughness to 0.6 nm, but this roughness is still larger than that for bare silica. Interestingly, Figure 1e looks very much like an image of bare silica, Figure 1f. However, the surface has an RMS roughness of 0.6 nm compared to 0.45 nm for bare silica, and the contact angle of water on the surface is still high at around 47−52°. It seems that the HMDS coating is relatively unperturbed by continual exposure to water and is stable for at least 7 days. This may indicate that HMDS chemically reacts with surface silanol groups on silica thus forming a robust layer. Solid state NMR experiments are currently being performed in an attempt to elucidate this.

An HMDS-coated MCM-41 sample (sample A) showed a decrease in BET surface area (1250 to 1049 $m^2 \cdot g^{-1}$) and in pore volume (0.98 to 0.75 $cm^3 \cdot g^{-1}$), consistent with the presence of the HMDS coating within the pores. The pore size distribution (data not shown) was not discernibly broadened due to the presence of the coating. The stability of six MCM-41 samples, all from the one synthesis batch (sample B), was investigated in distilled water and pH 6 phosphate buffer with and without HMDS-coating. It was observed that little change occurred in the measured XRD patterns for any of these samples after 12 days in either solution (Figure 2 and Table 2). However, nitrogen adsorption measurements on the uncoated MCM-41 samples before and after solution contact revealed a dramatic degradation of the structure, particularly after contact with the pH 6 buffer solution (Figure 3a). The pore diameter and pore volume values for the initial uncoated sample (shown in Table 2) were somewhat underestimated, because it was heated to 540 °C prior to measurement of its nitrogen adsorption isotherm. This resulted in a slight contraction of the structure, shown by a decrease in the $d_{100}$
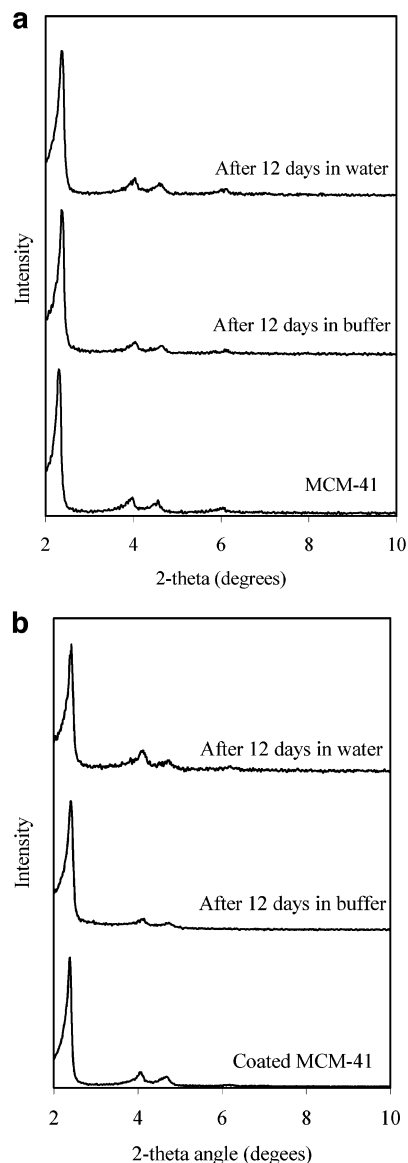


**Figure 2.** XRD patterns for MCM-41 following extended contact with solution: (a) uncoated MCM-41; (b) coated MCM-41. The intensities of the patterns for each sample after solution contact have been normalized with respect to the same sample prior to solution contact using the $d_{100}$ peak.

**Table 2. Summary of Results of Stability Tests on Coated and Uncoated MCM-41 in Solution**

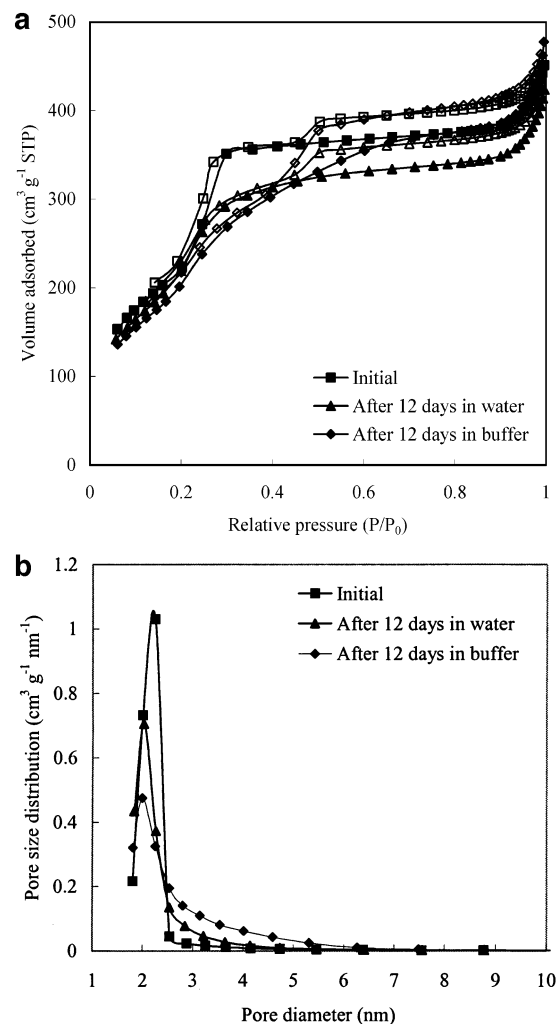| sample | XRD $d_{100}$ spacing (nm) | BET surface area ($m^2 \cdot g^{-1}$) | BJH pore diameter (nm) | pore volume ($cm^3 \cdot g^{-1}$) |
|---|---|---|---|---|
| initial uncoated | 3.8 | 908 | 2.7 | 0.67 |
| 12 days in water | 3.7 | 920 | 3.2 | 0.48 |
| 12 days in buffer | 3.7 | 563 | 6.7 | 0.41 |
| initial coated | 3.7 | 841 | 2.7 | 0.67 |
| 12 days in water | 3.7 | 839 | 2.8 | 0.63 |
| 12 days in buffer | 3.7 | 771 | 3.3 | 0.70 |

spacing (0.4 nm). Nonetheless, the BET surface area and the pore volume of the uncoated samples each decreased by about 40% relative to the initial uncoated sample after 12 days in buffer (Table 2). The BJH pore size distributions of the solution-treated samples no longer showed a narrow peak in the mesoporous range (Figure 3b). These results show that gas adsorption isotherms are more sensitive indicators of degradation of the pore structure of MCM-41 than XRD spectra, and so XRD alone should not be used to test material stability.
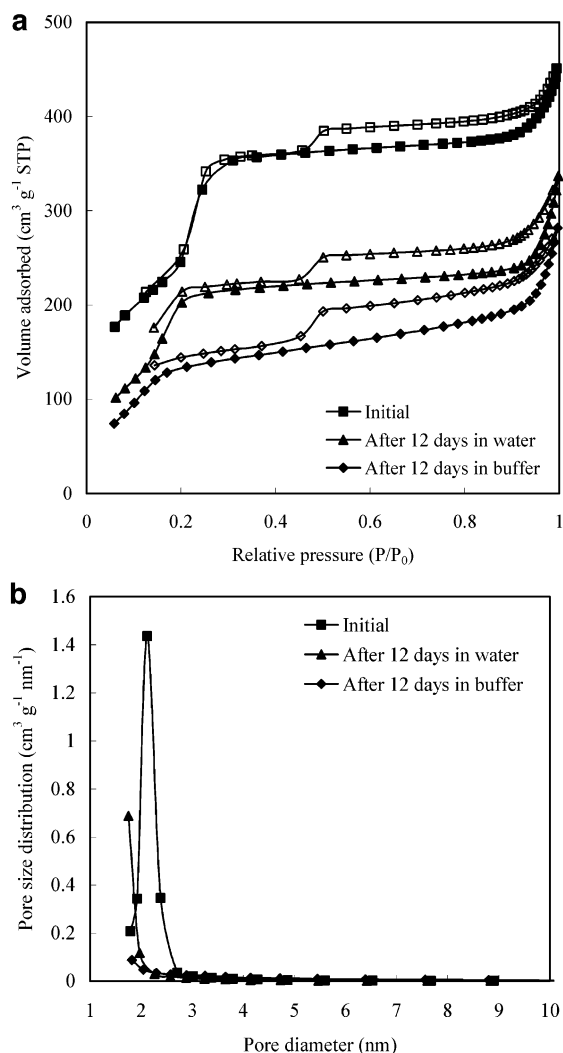
**Figure 3.** Nitrogen adsorption isotherms (a), and resultant BJH pore size distributions (b), for uncoated MCM-41 before and after solution contact. Filled symbols represent adsorption, and unfilled symbols represent desorption.



**Figure 4.** Nitrogen adsorption isotherms (a), and resultant BJH pore size distributions (b), for coated MCM-41 before and after solution contact. Filled symbols represent adsorption, and unfilled symbols represent desorption.

In contrast, the HMDS-coated MCM-41 samples (Figure 4) retained their high BET surface area in water and showed only a small decrease in surface area (8%) after 12 days in pH 6 buffer. The total pore volume of these samples was also not significantly changed by either solution treatment. The BJH pore size distributions did show slight broadening after solution treatment, more so for the buffer than distilled water. However the extent of the broadening was much less than that observed by Lim and Stein for a vinyl-functionalized MCM-41 sample after hydrothermal treatment, which also showed a significant increase in pore volume not seen here.[6] It is possible that the solution had an effect on the material properties in this work due to the coating being incomplete, allowing attack on the uncoated portions. In both cases the pH 6 buffer solution had a greater effect on the material's structure than did distilled water. As the solubility of silica is not expected to be altered by pH in the range studied (ca. 4–6) or by the presence of 50 mM salt,[31] the reason for this effect is unclear.

## Conclusions

Flat silica surfaces have been used to show that HMDS can be used to form a robust hydrophobic coating on silica relatively easily compared with silylation with TCMS. This is important for applications involving aqueous solutions because of the increased stability of the HMDS-coated materials in water. MCM-41 coated with HMDS retained its regular structure and uniform pore size according to XRD and gas adsorption measurements. The coated MCM-41 also showed much greater structural stability over 12 days in water or pH 6 phosphate buffer than uncoated MCM-41. Thus, HMDS-coated MCM-41 shows promise for applications involving extended contact with aqueous solutions, such as separation of proteins.

(31) Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons: New York, 1979.