

Modification of MCM-41 by Surface Silylation with Trimethylchlorosilane and Adsorption Study

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Siliceous MCM-41 samples were modified by silylation using trimethylchlorosilane (TMCS). The surface coverage of functional groups was studied systematically in this work. The role of surface silanol groups during modification was evaluated using techniques of FTIR and ^{29}Si CP/MAS NMR. Adsorption of water and benzene on samples of various hydrophobicities was measured and compared. It was found that the maximum degree of surface attachments of trimethylsilyl (TMS) groups was about 85%, corresponding to the density of TMS groups of 1.9 per nm^2 . The degree of silylation is found to linearly increase with increasing pre-outgassing temperature prior to silylation. A few types of silanol groups exist on MCM-41 surfaces, among which both free and geminal ones are responsible for active silylation. Results of water adsorption show that aluminosilicate MCM-41 materials are more or less hydrophilic, giving a type IV isotherm, similar to that of nitrogen adsorption, whereas siliceous MCM-41 are hydrophobic, exhibiting a type V adsorption isotherm. The fully silylated Si-MCM-41 samples are more hydrophobic, giving a type III adsorption isotherm. Benzene adsorption on all MCM-41 samples shows type IV isotherms regardless of the surface chemistry. Capillary condensation occurs at a higher relative pressure for the silylated MCM-41 than that for the unsilylated sample, though the pore diameter was found reduced markedly by silylation. This is thought attributed to the diffusion constriction posed by the attached TMS groups. The results show that the surface chemistry plays an important role in water adsorption, whereas benzene adsorption is predominantly determined by the pore geometry of MCM-41.

Introduction

The discovery of mesoporous molecular sieves, MCM-41,^{1,2} has resulted in a worldwide resurgence in mesoporous material synthesis for catalysis, adsorption/separation, environmental pollution control, and intrazeolite fabricating technology (for more information, see recent reviews^{3–6}). The most striking features of these novel materials, such as large BET surface area and pore volume, hydrophobic surface nature, etc., manifest itself as a selective adsorbent for the removal of volatile organic compounds (VOCs) presented in high-humidity gas streams or wastewater. Our previous studies^{7,8} indicated that adsorption characteristics of MCM-41 for polar molecules greatly depend on the concentrations of surface silanol groups (SiOH). It has been demonstrated^{7,9–12} that several types of SiOH groups exist over MCM-41 surfaces which can be qualitatively and quantitatively determined by a number of techniques such as solid-state ^{29}Si nuclear magnetic resonance with magic-angle spinning and cross polarization (^{29}Si CP/MAS NMR),⁷ Fourier transformation infrared (FTIR) spectroscopy,^{7,9–12} thermogravimetric analysis (TGA⁷), and temperature-programmed desorption (TPD) of pyridine,⁷ etc. It is those SiOH groups that enable the various successes in modification of MCM-41 for catalysis,^{13,14} adsorption,^{15,16} and novel composites.^{17,18} Mobil Oil Corporation has patented a sorption separation process using modified MCM-41 for purification of water.¹⁵ Feng et al.¹⁶ reported a functionalized mesoporous adsorbent for the removal of heavy metals from wastewater.

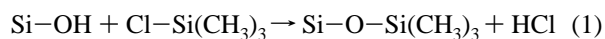
In our laboratory, a systematic study involving surface characterization, surface modification, and functionalization has

been carried out in order to develop new adsorbents/catalysts for the removal of VOCs.^{7,8,19} Surface modification can be conducted in a various ways¹⁵ such as silylation, esterification, and chemical depositions. Although modification of MCM-41 and similar mesoporous materials by silylation has been investigated previously,^{1,7,15,20} some problems, such as the role of surface SiOH groups, degree of silylation, and adsorption behaviors of those modified samples, still require a better understanding which the present work aims to provide.

Experimental Section

Materials. Two MCM-41 samples with the Si/Al ratios of ∞ (designated Si-MCM-41) and 15 (designated Na-MCM-41) were synthesized using a cetyltrimethylammonium chloride solution (25 wt %, Aldrich) as the template. The detailed synthesis procedures were reported elsewhere.²¹ Templates were removed by solvent extraction using 1 M chloric acid in diethyl ether solvent (solid:liquid = 1 g:100 mL) at room-temperature overnight.⁷ Extraction was sometimes repeated till no surfactants were observed by thermogravimetric analysis (TGA). Hydrophobic zeolite NaY (Si/Al = 300) was obtained by steaming and acid treatments of the parent NaY (Si/Al = 2.45, from CU Chemie Uetikon AG, The Netherlands) according to the methods described by Ward²² and Fleish et al.²³

Surface Modification with Trimethylchlorosilane (TMCS). It is well recognized that surface silylation of MCM-41 takes place through the reaction between TMCS and surface SiOH groups as follows^{1,7}



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A monolayer of trimethylsilyl (TMS) groups is thus covalently attached to the pore surface of MCM-41. Approximately 2 g of template-extracted MCM-41 was outgassed in a vacuum system with a residual pressure of less than 5×10^{-4} Torr at a temperature of 723 K for a given time and then subsequently soaked in a TMCS solution in toluene with a concentration of 5 wt % (solid:liquid = 1 g:50 mL) at 343 K under stirring for a desired time. The mixture was then extensively washed with toluene and acetone to rinse away any residual chemicals. Finally, the powder was dried at 323 K. The degree of silylation was determined by a number of parameters, such as outgassing temperature, concentration of TMCS in toluene, reaction time, and temperature.

X-ray Diffraction (XRD). MCM-41 samples before and after the modification were examined by XRD using a PW 1840 diffractometer (Philips) with Co K α radiation at 40 kV and 25 mA.

Nitrogen Adsorption. Nitrogen adsorption-desorption isotherms were measured at the liquid nitrogen temperature using a Nova 1200 analyzer (Quantachrome). Samples were outgassed at 553 K overnight before measurements. Surface areas were calculated using the BET model. Pore volumes were estimated at a relative pressure of 0.94, assuming full surface saturation of nitrogen. Pore size distributions were obtained using the BJH model.

Nuclear Magnetic Resonance (NMR). Solid-state ^{29}Si NMR spectra were obtained at 59.63 MHz on a Bruker MSL 300 spectrometer. Samples were spun at a frequency of 2.5 kHz in Bruker double-air-bearing probes. The cross-polarization (CP) contact time used in this study was 8 ms, which has proven⁷ to be long enough to permit full cross polarization for silicons to which hydroxyl groups are directly attached, as well as for silicons in the secondary attached TMS groups. Spectral contributions from silicons deeper in the lattice are strongly discriminated against in the CP experiment due to their prohibitively long Si-H distances.²⁴

Fourier Transform Infrared (FTIR) Spectroscopy. A Perkin-Elmer 2000 FTIR spectrometer equipped with MCT detector was used to record infrared spectra of the MCM-41 samples. The detailed experimental conditions were reported previously.⁷

Adsorption Measurements. Adsorption of both water and benzene was performed gravimetrically in an adsorption apparatus using a quartz spring (Wilmad Glass). The sensitivity of weight measurement is 0.01 mg. Before each measurement, a sample was outgassed at 473 K overnight. The residual pressure within the adsorption chamber was below 5×10^{-4} Torr. The vapor pressure for an adsorptive was measured using the capacitance manometer (MKS Baratron 122B) with a sensitivity of 0.1 Torr. Lower vapor pressures were also monitored using a silicon oil manometer (which were in excellent agreement with that measured by a pressure transducer). Adsorption equilibrium for water was normally achieved within 60 min, but at low vapor pressures (<1 Torr), 90 min was sometimes necessary. Adsorption equilibrium for benzene was reached within 20 min.

Results and Discussion

XRD. Shown in Figure 1 are the XRD patterns for the template-extracted Na-MCM-41 (a), the as-synthesized Si-MCM-41(b), the template-extracted Si-MCM-41 (c), and the fully silylated Si-MCM-41 (d) mesophases, together with the d_{100} spacings. It is seen that samples with different Si/Al ratios (a and b) synthesized using liquid crystal templates are well-

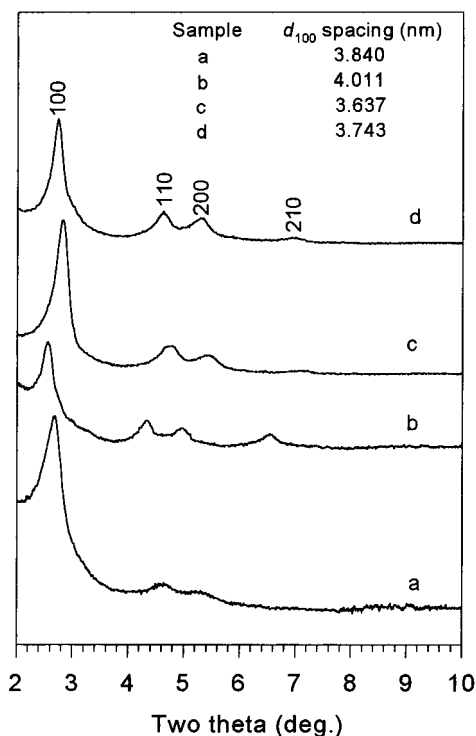


Figure 1. XRD patterns for template-free Na-MCM-41 (a), as-synthesized Si-MCM-41 (b), template-extracted Si-MCM-41 (c), and fully silylated Si-MCM-41 (d). Co K α ($\lambda = 0.179$ nm).

ordered mesoporous phases that can be indexed according to a hexagonal lattice,^{1,2} characteristic of MCM-41. The BET surface areas of these two MCM-41 samples were measured to be 1016 m²/g for sample a and 1180 m²/g for sample b. When the templates were removed by solvent extraction, the XRD pattern (c) is similar with that of the as-synthesized sample (b), but the intensities were considerably enhanced and the peak positions were shifted to higher 2θ (degrees) due to further condensation of silanols during extraction of templates, as is the case when templates were removed by calcination.^{21,25} As the template-free sample was fully silylated with TMCS, the X-ray diffractograms were highly resolved and the width of the main (100) peaks was narrowed, reflecting a better ordered pore structure. This is probably related to (1) the more homogeneous pore structures brought about by the chemical attachments of a monolayer of TMS groups over MCM-41 surfaces and/or (2) the unavailability of any residual waters due to the complete removal of SiOH groups during silylation since it has been found that adsorbed water molecules occluded inside the pores of MCM-41 have a significant impact on the intensity of the main (100) peak.²⁶

Nitrogen Adsorption. Shown in Figures 2 and 3 are the typical nitrogen adsorption-desorption isotherms and pore size distributions of MCM-41 samples before and after silylation, respectively. A sharp increase in the adsorption amount of nitrogen at the relative pressure of 0.3 can be seen for the sample before silylation, which is due to capillary condensation. The relative pressures of condensation for the partially and fully silylated samples are now at about 0.2 and 0.17, respectively. The knees for the silylated samples are not as steep as that before silylation, reflecting a relatively broad pore size distribution after silylation (see Figure 3). Hysteresis of type H3²⁷ can be observed on all the samples above the relative pressures of 0.42 which is attributed to the capillary condensation of the nitrogen within interparticles and/or some impurity phases, such as lamellar mesostructures frequently generated by liquid-templat-

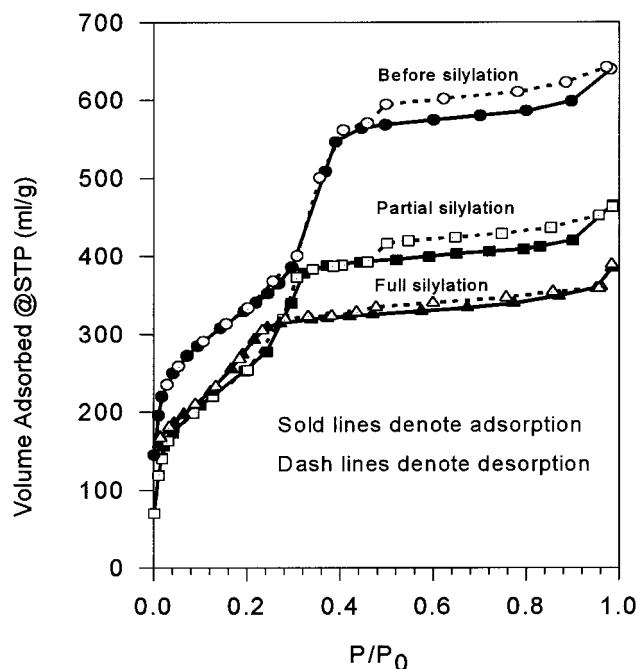


Figure 2. Nitrogen adsorption-desorption isotherms of Si-MCM-41 before and after silylation.

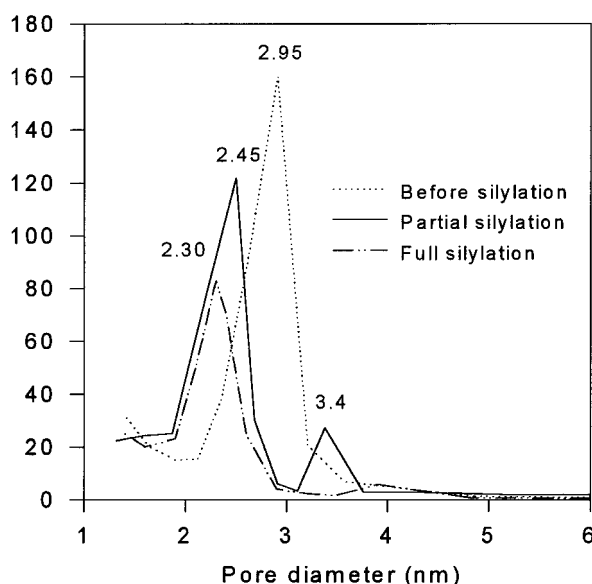


Figure 3. Pore size distributions of Si-MCM-41 samples before and after silylation

ing synthesis.²⁸ The fully silylated sample does not show a significant hysteresis which may be associated with particle aggregation during silylation. From Figure 3 it can be seen that the decrease in the pore diameter after the partial silylation is about 0.50 nm. A secondary peak at about 3.4 nm can also be observed. This peak is considered to generate as a result of calculating a small experimental error since no obvious change of adsorption amount of nitrogen at the corresponding P/P_0 region on the isotherms shown in Figure 2 could be found. For the fully silylated sample, the decrease in pore diameter is about 0.65 nm, which is fairly consistent with the theoretical prediction. As well documented,²⁹ the maximum lateral extension of a TMS group is roughly 0.37 nm. Assuming a monolayer of TMS groups was formed over MCM-41 surfaces after silylation, the reduction of pore diameter should, therefore, be about 0.74 nm. The difference of 0.09 nm between the theoretical and

TABLE 1: Influence of Pre-outgassing Temperature on the Degree of Silylation over MCM-41 Surfaces^a

sample	outgassing temp (K)	BET surf. area (m ² /g)	pore vol (mL/g)	BJH pore diam (nm)	surf. coverage ^b
a		1180	0.91	2.95	
b	373	887	0.79	2.69	30
c	473	802	0.66	2.54	44
d	573	753	0.62	2.45	43
e	673	631	0.50	2.33	71
f	723	633	0.45	2.30	85
g	773	612	0.46	2.30	85

^a Silylation was conducted at 343 K using a TMCS solution in toluene with a concentration of 5% and in a ratio of solid to liquid of 1 g:25 mL. The silylation temperature and concentration were found to be the optimal parameters. ^b All values $\times 100$.

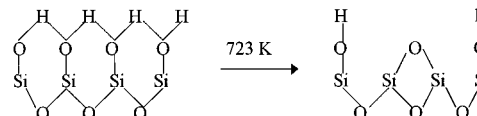


Figure 4. A scheme of dehydroxylation processes among hydrogen-bonded silanols during which extra free silano groups are generated.

BJH calculations is suggested to be associated with the heterogeneity of attached TMS groups with a surface coverage of about 85% (see below).

Surface Coverage of TMS Groups. As mentioned above, the degree of silylation can be affected by parameters such as pre-outgassing temperature, silylation temperature, and concentration of a silylating agent. A systematic study of the surface coverage as a function of pre-outgassing temperature was carried out (Table 1). The surface coverage of TMS groups was calculated based on the following equation as reported previously:⁷

$$S = \frac{\Delta W\% \times N_A}{\text{EMW} \times S_{\text{BET}}} \times 10^{-20} \text{ (number/nm}^2\text{)} \quad (2)$$

where S is the number of attached TMS groups per nm², $\Delta W\%$ represents the weight gain after silylation (%), N_A is Avogadro's number, EMW is the effective molar weight of the attached TRMS groups (72 g/mol), and S_{BET} is the BET surface area (m²/g), assuming that each TMS group occupies a cylindrical volume of 0.43 nm^{2.28} and the external surface areas are negligible. It can be seen from Table 1 that the degree of silylation over MCM-41 surface has a linear relationship with the pre-outgassing temperature between 373 and 723 K. The maximum coverage found in this study was about 85%, which corresponds to the number of attached TMS groups of 1.9 per nm².

Role of Surface SiOH Groups. Our recent study⁷ demonstrated that the density of SiOH groups (including free, hydrogen-bonded, and geminal) over a template-extracted MCM-41 sample is about 3.0 per nm². It is only the free and geminal SiOH groups that are the active sites to react with TMCS, while hydrogen-bonded ones are not because of the hydrophilic networks formed among themselves. Therefore, increasing the density of free SiOH groups would increase the degree of silylation. It was also found that the population of free SiOH groups can be increased by increasing outgassing temperature because dehydroxylation among hydrogen-bonded SiOH groups results in the loss of water. The simultaneous generation of free SiOH groups and siloxane bridges is schematically shown in Figure 4. Dehydroxylation from geminal SiOH groups is thought to be very difficult since silicon does not form a siloxane link ($=\text{Si}=\text{O}$) readily.³⁰ The

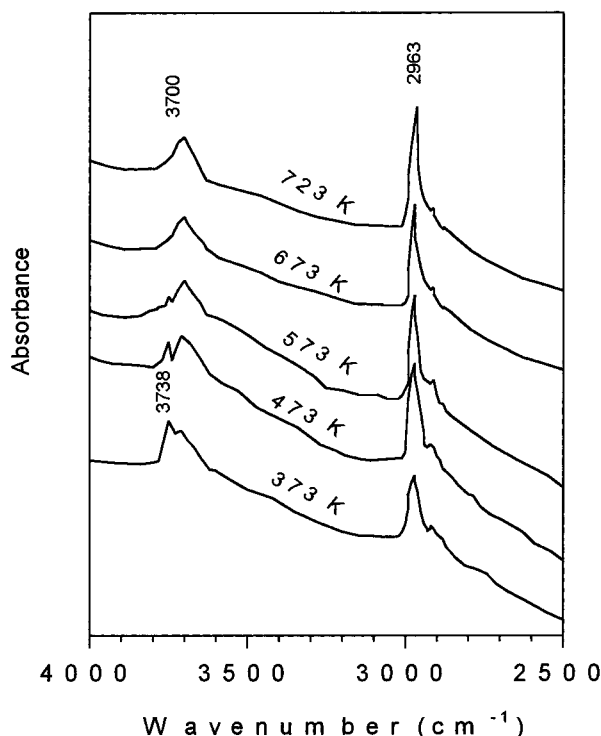


Figure 5. FTIR spectra of Si-MCM-41 samples silylated after outgassing at different temperatures. All samples were outgassed at 723 K prior to spectrum measurements.

outgassing temperatures between 673 and 723 K were found to be the reasonable range in which a maximum density of free SiOH groups can be obtained and thus a high degree of silylation.

Shown in Figure 5 are the FTIR spectra of MCM-41 samples silylated with different pre-outgassing temperatures. The spectra were recorded after samples were outgassed at 723 K in situ in order to see whether free SiOH groups still exist over silylated MCM-41 surfaces or not. It can be seen that a sharp absorption band at 2963 cm^{-1} and a small shoulder peak at 2920 cm^{-1} , attributed to the attached TRMS groups, appeared. The intensities of the main peak were increased with increasing pre-outgassing temperature because more and more accessibly free SiOH groups available for TMCS were generated with increasing pre-outgassing temperature as shown in Figure 4. This is consistent with the results in Table 1. The intensities of the absorption band at 3738 cm^{-1} , ascribed to the free SiOH groups, were decreased and at last disappeared with increasing pre-outgassing temperature. These free SiOH groups originated from the hydrogen-bonded SiOH groups due to dehydroxylation at 723 K prior to FTIR measurements, not the original free SiOH groups. The intensity for the absorption band at 3700 cm^{-1} remains constant regardless of pre-outgassing temperature. This band has been assigned to the secondary free SiOH groups derived from the geminal silanols⁷ (corresponding to the silicon sites of b' in the following NMR spectra, Figure 6) and/or the inside lattice SiOH groups.³¹

Figure 6 shows the typical ^{29}Si CP/MAS NMR spectra for the siliceous MCM-41 samples with and without surface attachments of TMS groups, also with the chemical shift assignments for the observable resonances. Three resonances at -110, -101, and -92 ppm which are assigned to the silicon sites of Q^4 , $^*\text{Si}(\text{OSi})_4$ (a), Q^3 , $\text{HO}^*\text{Si}(\text{OSi})_3$ (b), and Q^2 , $(\text{HO})_2^*\text{Si}(\text{OSi})_2$ (c), respectively, can be observed on the template-extracted MCM-41. The Q^3 sites are associated with the isolated SiOH groups (i.e., free and hydrogen-bonded), and

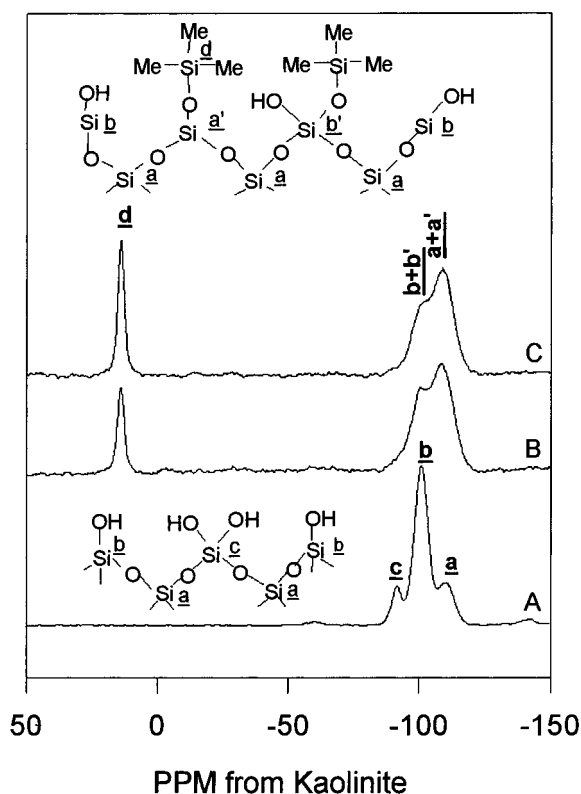


Figure 6. ^{29}Si CP/MAS NMR spectra for template-extracted Si-MCM-41 (A), partially silylated Si-MCM-41 with a coverage of 43% (B), and fully silylated MCM-41 (C).

the Q^2 sites correspond to the geminal silanols. For the two silylated samples in different degrees, a sharp peak at 14 ppm, ascribed to the attached silicon sites in TMS groups (d), is seen besides those obtained on the sample before silylation. The intensity for the Q^4 silicons ($a + a'$) is drastically increased at the expense of Q^3 silicons because these silicon sites were redistributed during silylation. The Q^2 sites for both the partially and fully modified MCM-41 samples are actually featureless in the ^{29}Si CP/MAS NMR spectra, demonstrating that geminal silanols are not hydrogen-bonded and are also the active sites for silylation as well. These NMR results reveal that both free and geminal SiOH groups are highly accessible to the silylation agent, TMCS.

Adsorption Study. Figure 7 shows the adsorption isotherms of water on various MCM-41 samples, together with the hydrophobic zeolite NaY for comparison. The adsorption isotherm on Na-MCM-41 is of type IV,²⁷ similar to that of nitrogen adsorption, indicating that aluminosilicate MCM-41 materials are more or less hydrophilic. The static electric field formed between tetrahedral Al and sodium is responsible for water adsorption. The adsorption isotherm over the Si-MCM-41 sample is type V, indicating a weak interaction of water with the siliceous MCM-41 surfaces. Water adsorption over siliceous MCM-41 probably took place via hydrogen bonding between the SiOH groups and water molecules. A steep rise in adsorption for both Na-MCM-41 and Si-MCM-41 is also observed which is due to the volume fillings of the mesopores³² or to a cooperative condensation mechanism.¹¹ The adsorption isotherm on the fully silylated Si-MCM-41 sample is of type III without any observation of pore filling or capillary condensation, similar to that of water adsorption on hydrophobic zeolite NaY, demonstrating that the surface-modified siliceous MCM-41 is more hydrophobic than before silylation. The small amount of adsorbed water possibly occurred at the residual SiOH

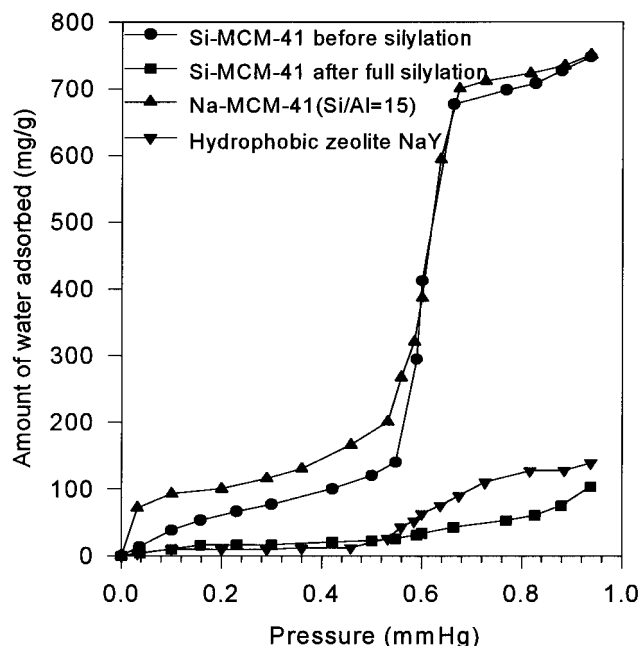


Figure 7. Water adsorption isotherms of various samples at 295 K.

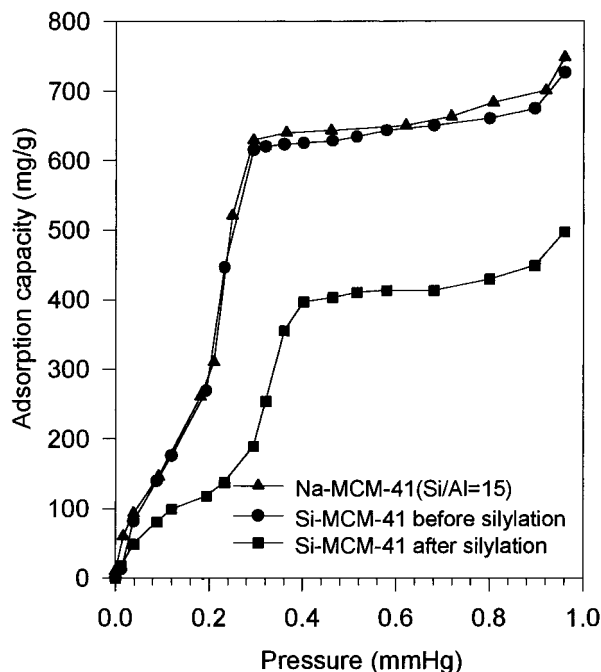


Figure 8. Benzene adsorption isotherms of various MCM-41 at 295 K.

sites through hydrogen bonding and/or the strained siloxane bridges by rehydroxylation.

Shown in Figure 8 are the benzene adsorption isotherms over the Na-MCM-41 and Si-MCM-41 samples before and after the modification. All isotherms are of type IV with a initial monolayer adsorption at the low P/P_0 , revealing an organophilic property of MCM-41 materials. The P/P_0 where the amount of benzene adsorbed increases suddenly is lower for the Na-MCM-41 and Si-MCM-41 samples than for the fully silylated Si-MCM-41 sample. This is unexpected since the mesopore diameter of the silylated Si-MCM-41 is smaller than that of the original sample (see Figure 3). One explanation could be that adsorption of benzene over the modified MCM-41 sample is significantly determined by the pore configuration. Diffusion resistance posed by attachment of TMS groups is the key

parameter in controlling the pore-filling process of benzene, rather than the surface chemistry.

The above adsorption results demonstrate that a surface-modified MCM-41 is very hydrophobic without significant adsorption of water in the whole vapor pressure range, but with a good capability of adsorbing organic compounds. This is of particular importance in designing selective adsorbents for environmental applications, such as the removal of VOCs in the presence of high humidity and adsorption of organics from wastewater. Further studies concerning adsorption kinetics, measurements of breakthrough curves for a real VOC stream, and isotherm measurements of typical organic compounds are in progress.

Conclusion

The surface chemistry of MCM-41 can be effectively modified to be more hydrophobic by chemical attachment of organic species (silylation). The free and germinal silanol groups over MCM-41 surfaces are responsible for such active modification. The silylation process can be enhanced by pre-heat treatment, and a maximum surface coverage of TMS groups can be achieved. Water adsorption isotherms show that surface-modified MCM-41 samples are very hydrophobic without any observation of pore fillings or capillary condensation. However, capillary condensation of benzene on all MCM-41 samples occurred regardless of surface chemistry. It is suggested that the surface chemistry of MCM-41 plays an important role in water adsorption, while the pore configuration is more important in affecting benzene adsorption. The results of this study demonstrated that surface modification of MCM-41 by silylation is an effective technique in tailoring selective adsorbents for the removal of organic compounds from streams or wastewater.

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