

Comprehensive Study of Surface Chemistry of MCM-41 Using ^{29}Si CP/MAS NMR, FTIR, Pyridine-TPD, and TGA

X. S. Zhao,[†] G. Q. Lu,^{*,†} A. K. Whittaker,[‡] G. J. Millar,[§] and H. Y. Zhu[†]

Department of Chemical Engineering, Center for Magnetic Resonance, and Department of Chemistry, The University of Queensland, Qld 4072, Australia

Received: April 21, 1997; In Final Form: June 6, 1997[®]

A comprehensive study was conducted on mesoporous MCM-41. Spectroscopic examinations demonstrated that three types of silanol groups, i.e., single, $(\text{SiO})_3\text{Si}-\text{OH}$, hydrogen-bonded, $(\text{SiO})_3\text{Si}-\text{OH}-\text{OH}-\text{Si}(\text{SiO})_3$, and geminal, $(\text{SiO})_2\text{Si}(\text{OH})_2$, can be observed. The number of silanol groups/nm², α_{OH} , as determined by NMR, varies between 2.5 and 3.0 depending on the template-removal methods. All these silanol groups were found to be the active sites for adsorption of pyridine with desorption energies of 91.4 and 52.2 kJ mol⁻¹, respectively. However, only free silanol groups (involving single and geminal silanols) are highly accessible to the silylating agent, chlorotrimethylsilane. Silylation can modify both the physical and chemical properties of MCM-41.

Introduction

Mesoporous molecular sieve, MCM-41 (a member of the M41S family)^{1,2} possesses hexagonally arranged uniform pore structures. The important characteristics of this novel material are its large BET surface area, high porosity, controllable and narrowly distributed pore sizes that manifest itself as a very promising candidate as catalyst or catalyst support,^{3–6} adsorbent,^{7–9} and host for host–guest encapsulation to develop advanced composite materials.^{10,11} Furthermore, it is expected that surface-modified MCM-41 may find other applications, such as in chromatographic separation and/or membrane-based gas separation.

A preliminary study indicated that the adsorption capacity of MCM-41 for polar molecules (e.g., H₂O, methanol) at a relatively low vapor pressure was, to a large extent, related to the density of surface silanol groups (SiOH),¹² which are also responsible for ion exchange¹³ and postmodification, such as silylation^{2,14} and chemical deposition.¹⁵ It is, therefore, desirable to evaluate the surface chemistry of MCM-41 qualitatively and quantitatively in terms of its SiOH groups.

Fourier transformation infrared (FTIR) spectroscopy has been extensively used in previous studies^{14,16–18} to investigate the surface nature of MCM-41. Ishikawa et al.¹⁶ recently studied the types and concentrations of SiOH groups over mesoporous silica FSM-16 (characteristics of MCM-41) using FTIR and gravimetric methods. Both free and hydrogen-bonded SiOH groups, with O–H vibration stretching bands at 3740 and 3600–3500 cm⁻¹, respectively, were observed and the number of SiOH groups per nm², α_{OH} , was determined to be 3.3. Llewellyn et al.¹⁷ reported that the interaction of water with aluminosilicate MCM-41 and concluded that the α_{OH} was 1.2. Jentys et al.¹⁸ reported that besides surface SiOH groups, inside the lattices, SiOH groups can also be detected which gives an IR absorbance at 3715 cm⁻¹. Though widely used, FTIR cannot discriminate between single and geminal SiOH groups.

Solid-state ^{29}Si nuclear magnetic resonance (^{29}Si NMR) experiments employing magic-angle spinning (MAS) with or

without cross polarization (CP) has been shown previously to be reliable means for quantitatively characterizing the nature of various solid surfaces,^{19–22} in particular that of amorphous silica.^{20–22} The fact that the CP process discriminates against ^{29}Si nuclei far away from protons makes this technique a sensitive method for measuring SiOH groups. Relaxation studies in both the literature^{21a,c,e} and this work have shown that the resonances of those silicons to which OH groups are directly connected, and silicons in the attached silane groups (e.g., $\text{Si}(\text{CH}_3)_3$) can be measured quantitatively. By measuring ^{29}Si CP/MAS NMR spectra, geminal and single SiOH groups can be discriminated as Q² and Q³ silicon sites, respectively. In addition, the intensities of those silicons which are used for quantitative analysis are not affected by the presence of water molecules,^{21b} and therefore preparation of a completely anhydrous sample is not a prerequisite.

Temperature-programmed desorption (TPD) of pyridine is another potential method for determining the distribution of energetically heterogeneous SiOH sites over silica surfaces.^{23–26} The lone-pair electrons of the nitrogen atom in the pyridine ring interact strongly with surface SiOH groups through hydrogen bonding.²⁵ Different types of SiOH groups (free and hydrogen-bonded) exhibit different activation energies of desorption and thus can be differentiated.

In the present study, the techniques of ^{29}Si CP/MAS NMR and pyridine-TPD which have not been used to study MCM-41 surfaces so far, combined with FTIR and other methods are used to examine the surface chemistry of a number of siliceous MCM-41 samples. The aims of this work are (1) to gain a comprehensive understanding of the surface chemistry of MCM-41, (2) to provide further insights into the parameter, α_{OH} , and (3) to study the effectiveness of new alternative methods, such as ^{29}Si CP/MAS NMR and pyridine-TPD for characterizing MCM-41 surfaces.

Experimental Section

Synthesis of MCM-41. Siliceous MCM-41 was synthesized using 25% cetyltrimethylammonium chloride (CTACl, Aldrich) as a template with the following molar ratios 3.6 Na₂O:30 SiO₂:5.1 CTACl:690 H₂O. The detailed synthesis procedure was reported elsewhere.²⁷ The resultant materials were filtered, washed extensively with deionized water, and dried at 323 K in air.

* To whom correspondence should be addressed.

[†] Department of Chemical Engineering.

[‡] Center for Magnetic Resonance.

[§] Department of Chemistry.

[®] Abstract published in *Advance ACS Abstracts*, August 1, 1997.

TABLE 1: Characterization Results for Various MCM-41 Samples^a

sample	I_{100} (au)	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	V_{internal} (cm ³ /g)	V_{external} (cm ³ /g)	d_{BJH} (Å)	C_{BET}	uptake (wt %) of	
								water	benzene
MCM-41(C)	109	1180	0.88	0.68	0.20	29.4	115	3.9	14.0
MCM-41(C) silylated with TRMS	103	928	0.64	0.54	0.10	25.3	45	2.0	13.1
MCM-41(E)	94	1153	0.85	0.60	0.25	30.0	131	4.5	9.7
MCM-41(E) silylated with TRMS	94	829	0.60	0.51	0.09	24.0	52	2.2	9.7

^a I_{100} : relative intensity of peak [100] compared to the as-synthesized MCM-41 sample. S_{BET} : surface area calculated by BET model. V_{total} : total pore volume estimated at a relative pressure of 0.94, assuming full surface saturation. V_{inter} : internal pore volume obtained from t -plot.²⁸ V_{exter} : external pore volume, $V_{\text{exter}} = V_{\text{total}} - V_{\text{inter}}$. D_{BJH} : pore diameter calculated from BJH model.

Treatment of MCM-41. Template removal was conducted by either calcination or extraction. Calcination was performed in a muffle furnace at 813 K for 24 h in air. Extraction was carried out in 1 M HCl solution in diethyl ether (solid:liquid = 1 g:100 mL) at room temperature overnight. Samples for which templates were removed by calcination and extraction are denoted as MCM-41(C) and MCM-41(E), respectively. Modification of MCM-41 was conducted by the following procedure. Approximately 2 g of template-free MCM-41 sample was dried in a vacuum system at 383 K for 24 h until the weight became constant (W_1) and then subsequently soaked in a chlorotrimethylsilane solution in toluene at a fixed concentration (solid:liquid = 1 g:5 mL) at ambient temperature under stirring for a desired time. The mixture was then extensively washed with acetone and air-dried. Finally, the powder was dried again in vacuum at 383 K until the weight became constant (W_2). The weight gain ($\Delta W\%$) after silylation was calculated by $\Delta W\% = (W_2 - W_1) \times 100$.

X-ray Diffraction (XRD). XRD data were obtained using a PW 1840 diffractometer (Philips), Co K α radiation, Fe filter.

Nitrogen Adsorption. Nitrogen adsorption-desorption isotherms were measured at 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, while internal and external pore volumes were derived from an improved MP method.²⁸ Pore diameters were calculated using the BJH model.

Thermogravimetric Analysis (TGA). Calcination, dehydration, and dehydroxylation processes were evaluated by a TGA (Shimadzu TGA-50) technique. About 10 mg of the as-synthesized MCM-41 was placed in a platinum pan and heated from room temperature to 1273 K at a heating rate of 2 K/min in air with a flow rate of 150 mL/min.

Evaluation of Hydrophobicity of MCM-41. The hydrophobicity of MCM-41 was evaluated by measurements of water and benzene adsorption capacities, also with the TGA.²⁹ Before adsorption, about 10 mg of template-free MCM-41 sample was activated in situ at 383 K in the presence of high-purity helium with a flow rate of 140 mL/min to remove physically adsorbed water and then cooled to 298 K. At this temperature, an adsorbate (either benzene or water) was introduced from a bubbler by high-purity nitrogen at a concentration of 2000 ppm for benzene and 1% for water, respectively. The total flow rate was 200 mL/min balanced by helium. Equilibrium adsorption capacity was then calculated from the weight gain data.

Temperature-Programmed Desorption of Pyridine (Pyridine-TPD). Pyridine-TPD curves were obtained by using the TGA. About 10 mg of template-free MCM-41 sample was activated in situ at 573 K overnight in the presence of 140 mL/min helium and then cooled to 325 K. At this temperature, pyridine was alternatively introduced by a nitrogen flow from a bubbler as mentioned above until constant weight was observed. Temperature was then linearly increased to 825 K

with various heating rates. Desorption of pyridine was plotted as the first derivative TG (DTG).

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. Powdered materials were pressed into a tungsten mesh grid and installed in an in situ FTIR transmission cell of the type described by Yates and co-workers.³⁰ Samples were flushed with ultrahigh-purity helium for 1 h prior to analysis. An Eurothem temperature controller (Model 904) was then used to linearly heat the MCM-41 to the desired temperature for recording spectra. Spectra were acquired at 4 cm⁻¹ resolution and averaged over 64 scans. Manipulation of spectra data was achieved by the use of Grams research software.

Nuclear Magnetic Resonance (NMR). Solid-state ²⁹Si 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 CP contact time used in this study was 8 ms which has been proven to be long enough to permit full cross polarization for silicons to which hydroxyl groups are directly attached, as well as silicons in the secondary attached TRMS groups (see below). Spectral contributions from silicons deeper in the lattice are strongly discriminated against in the CP experiment due to their prohibitively long Si-H distances.^{21a} As a consequence, the intensities of the signals from the isolated and geminal silanols and the attached silane groups are believed to be reliable and valid.

Results

Characterization of MCM-41 Samples. The properties of the as-synthesized MCM-41, as well as the samples with various treatments were examined by X-ray diffraction, N₂ adsorption, and vapor adsorption measurements as listed in Table 1. The XRD pattern for the as-synthesized sample exhibits a strong [100] reflection peak with two small peaks, characteristics of MCM-41 material. After the template was removed by calcination, the intensity of [100] diffraction was slightly increased while the peak position was shifted to the low-angle region as previously observed.²⁶ This indicates that proper calcination leads to a better-defined structure of MCM-41 and a slight shrinkage in pore size due to the condensation of SiOH groups. When templates were removed by extraction, both BET surface area and the total pore volume show no significant changes. However, the intensity of the [100] reflection was slightly decreased, the internal pore volume decreased, and the external pore volume increased. This may be due to the partial depolymerization of the silica wall and decomposition of aggregated particles during the solvent-extraction process. When these two template-free samples were modified by silylation, the BET surface area, total pore volumes, and average pore sizes were all decreased. Benzene sorption capacities were slightly decreased (about 15% reduction). However, water

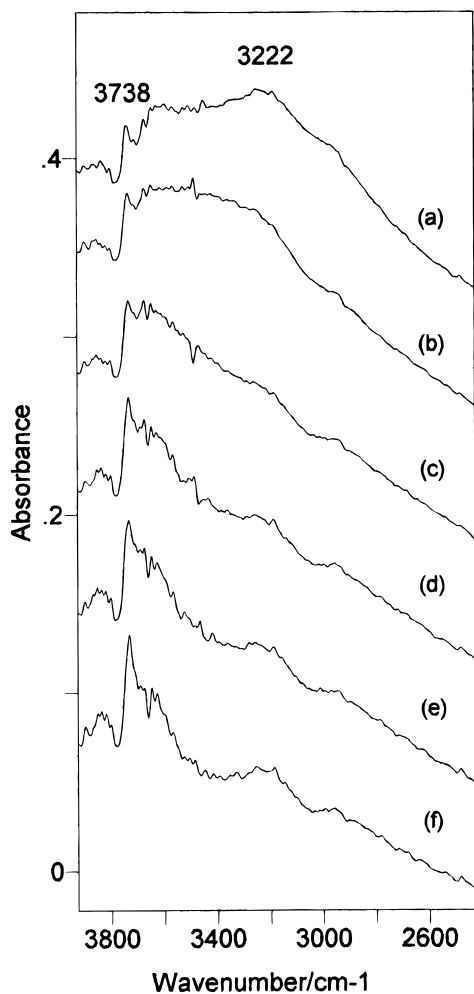


Figure 1. FTIR spectra for the sample of MCM-41(C) outgassed at different temperatures: (a) room temperature; (b) 373; (c) 473; (d) 573; (e) 673; (f) 773 K.

sorption capacities were significantly decreased by about 50%, reflecting a more hydrophobic surface. Table 1 also shows that the BET constants C for MCM-41 samples after the modification were decreased markedly, demonstrating that the surfaces become more hydrophobic compared to that before modification.²⁸ Because BET C is related to adsorption heat by $Q_{\text{ads}} = RT \ln C$, the polar N_2 molecules due to a quadrupole are expected to be adsorbed strongly by more hydrophilic surfaces, and thus a larger adsorption heat and vice versa.

FTIR Investigation. Figure 1 shows the FTIR spectra of sample MCM-41(C) in the range 4000–2500 cm^{-1} evaluated at different temperatures. At room temperature, a sharp absorption band at 3738 cm^{-1} ascribed to free SiOH groups^{14,16–18} and another very broad absorption band centered at 3222 cm^{-1} , assigned to hydrogen-bonded SiOH groups perturbed by physically adsorbed water,^{14,16} respectively, are observed. With increasing outgassing temperature, the intensity of the absorption band at 3738 cm^{-1} was increased, while the intensity of the broad absorption band was decreased and shifted to higher wavenumbers because of dehydration and dehydroxylation at high temperatures in vacuo.

Figure 2 represents the FTIR spectra of the silylated MCM-41(C) samples outgassed at different temperatures. First, the absorption band at 3738 cm^{-1} disappeared. Second, the broad absorption band (now centered at 3430 cm^{-1} rather than 3222 cm^{-1}) can still be seen with an intensity similar to that of the sample before modification. Third, two new absorption bands at 2963 and 3700 cm^{-1} , respectively, can be observed. The

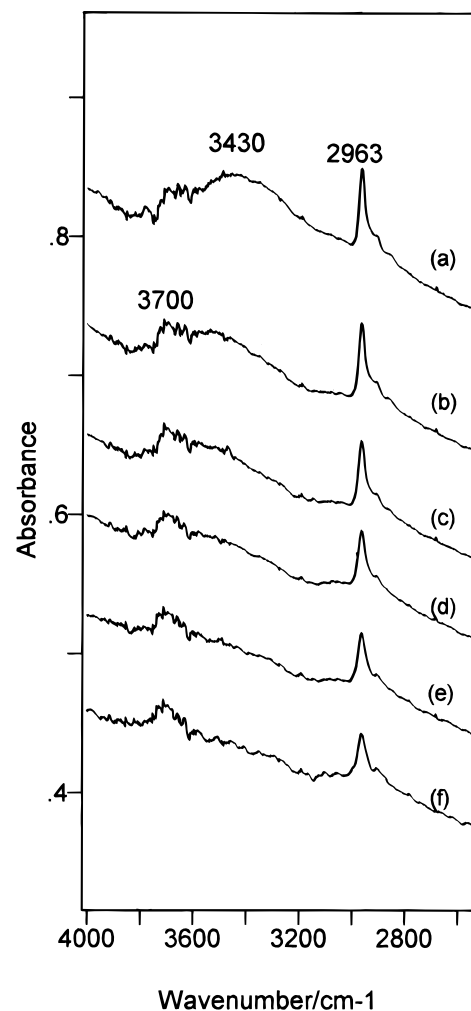


Figure 2. FTIR spectra of silylated MCM-41(C) outgassed at different temperatures: (a) room temperature; (b) 373; (c) 473; (d) 573; (e) 673; (f) 773 K.

first absorption band is ascribed to the attached trimethylsilyl (TRMS) groups,^{14a} and we assign the last absorption band to the single SiOH groups which was derived from the geminal SiOH groups during silylation, i.e., $(\text{CH}_3)_3\text{SiO}-\text{Si}-\text{OH}$. These results demonstrate that free SiOH groups are highly accessible to the silylating agent, chlorotrimethylsilane, while hydrogen-bonded SiOH groups are not.

Pyridine-TPD Study. Representative pyridine-TPD curves of MCM-41(C) samples collected with different heating rates are shown in Figure 3. These curves are expressed as the first derivative weight loss (DrTGA) against temperature. Two desorption peaks appear in the temperature range 323–523 K, as observed for amorphous silica before.²³ Since the MCM-41 sample was calcined at 823 K in situ until no weight loss occurred, the two peaks can be surely ascribed to pyridine desorptions from two energetically different adsorption sites. According to the literature,^{23–26} the first peak, at about 323–373 K corresponds to the desorption of pyridine from hydrogen-bonded SiOH groups, and the second peak, at about 393–443 K is associated with the desorption of pyridine from free SiOH groups. An energetic analysis using the model proposed by Cvetanovic and Amenomiya^{24c} (eq 1) enables us to obtain the activation energies of the two adsorption sites:

$$2 \ln T_m - \ln \beta = \frac{E_d}{RT_m} + \ln \frac{E_d}{AR} \quad (1)$$

Where T_m is the temperature (K) at which the maximum

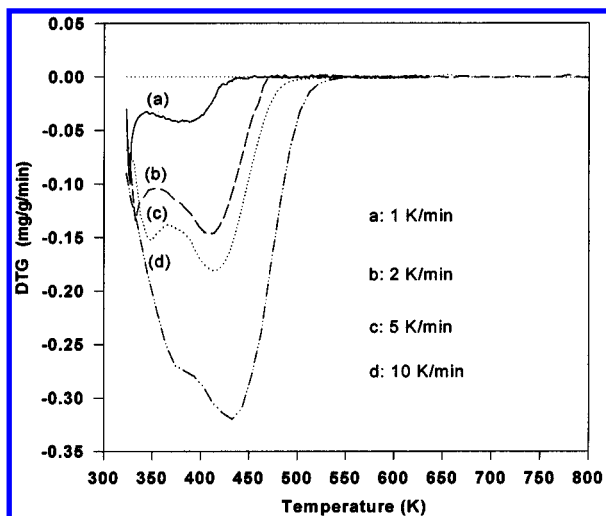


Figure 3. Pyridine-TPD profiles for the sample of MCM-41(C) desorbed at different heating rates.

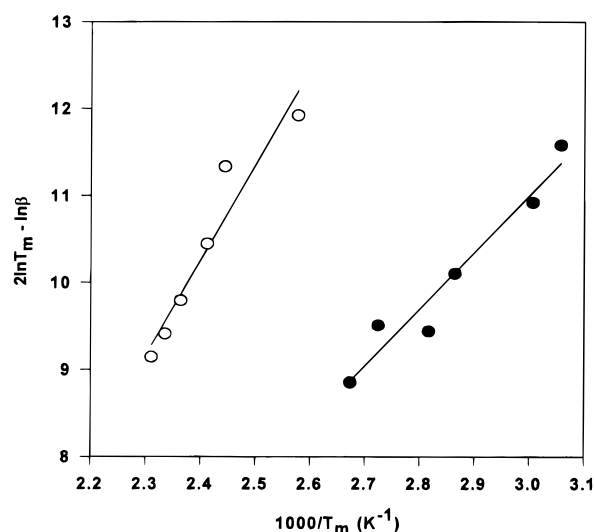


Figure 4. Plot of $\ln(T_m^2/\beta)$ as a function of $1/T_m$: (○) free silanol sites; (●) hydrogen-bonded silanol sites.

desorption rate for a given adsorption site is found, β is the heating rate (K/min) during desorption, E_d is the activation energy of the desorption sites, R is the gas constant, and A is the preexponential factor. The plots of $(2 \ln T_m - \ln \beta)$ as a function of $1/T_m$ for the two different desorption sites are shown in Figure 4. Two types of silanol sites (free and hydrogen-bonded silanols) are distinguished by their different activation energies of desorption. The calculated results are 54.2 and 91.4 kJ/mol for hydrogen-bonded and free SiOH groups, respectively, which are similar to the well-documented results on silica.²³

²⁹Si CP/MAS NMR Study Using Silylation as a Probe.

¹H-²⁹Si cross-polarization experiment restricts detection of an NMR signal to silicon nuclei that are near protons, i.e., at or near the surface. Therefore, ²⁹Si CP/MAS NMR is a sensitive and reliable technique for quantitative determination of SiOH groups on solid surfaces. However, before this technique can be used as a quantitative analysis method, the ¹H-²⁹Si cross-polarization dynamics should be examined to guarantee reliable quantitative interpretation.

Figure 5 shows the logarithmic intensity ($\log I$) of each of the three ²⁹Si CP/MAS NMR signals of the silylated MCM-41-(C) sample as a function of the cross-polarization contact times. With an increase in contact time, the intensities of the peaks due to the three silicon sites increase, to a maximum at about 5 ms, and then decrease. Most importantly, the slopes of the

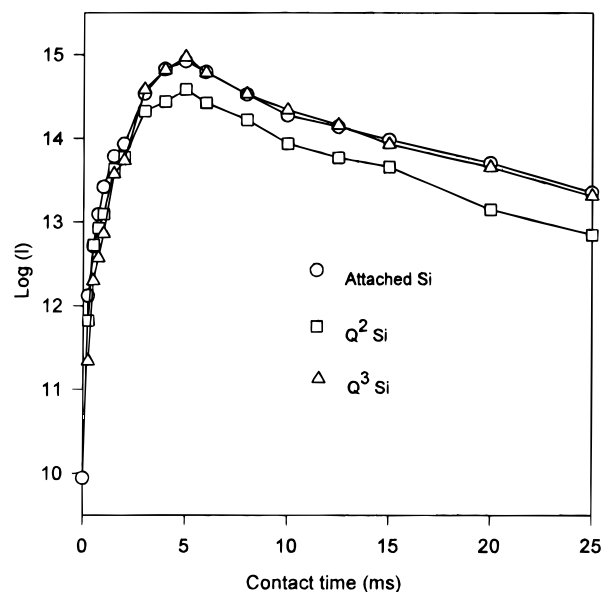


Figure 5. ¹H-²⁹Si cross polarization dynamics for three silicon sites.

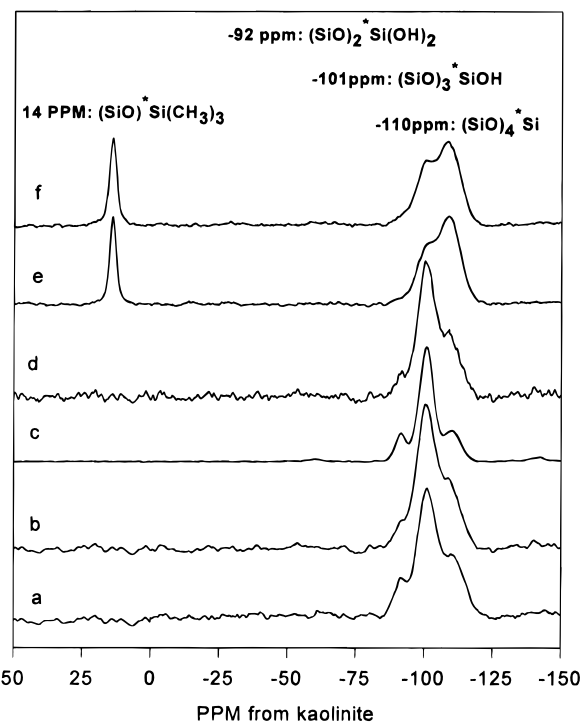


Figure 6. ²⁹Si CP/MAS NMR spectra for various siliceous MCM-41 samples together with amorphous silica for comparison: (a) amorphous SiO₂ used as silicon source for preparation of MCM-41; (b) the as-synthesized MCM-41; (c) MCM-41(E); (d) MCM-41(C); (e) sample c after silylation with TRMS; (f) sample d after silylation with TRMS.

plots of $\log I$ versus contact time are almost identical for each silicon type at long times, indicating a uniform ¹H T_{1ρ} and hence quantitative peak intensities in spectra collected using a contact time of 8 ms. The same experiment was also performed for the unsilylated MCM-41(C), and it was confirmed that quantitative spectra were also obtained for this sample. Sindorf and Maciel^{21c} have also studied silica surfaces and concluded that resonances of those silicons to which SiOH groups are directly attached and the resonance associated with attached silicon species, -Si(CH₃)₃ in ²⁹Si CP/MAS NMR spectra are suitable for quantitative analysis.

Figure 6 shows the ²⁹Si CP/MAS NMR spectra for MCM-41 samples treated using various methods, together with the spectrum for amorphous silica used as the silicon source for

TABLE 2: Relative Peak Areas (%) in the ^{29}Si CP/MAS NMR Spectra of Various MCM-41 Samples, as Well as the Amorphous Silica Used as Si Source for Synthesis^a

sample	Q ² sites: (SiO) ₂ *Si(OH) ₂	Q ³ sites: (SiO) ₃ *SiOH	Q ⁴ sites: (SiO) ₄ *Si	trimethylsilyl sites: (SiO) ₃ *Si(CH ₃) ₃
amorphous SiO ₂	14.7	59.2	26.1	
as-synthesized MCM-41	5.2	68.9	26.0	
MCM-41(C)	4.8	64.3	30.9	
MCM-41(C) silylated with TRMS	3.3 (2.6)	38.3 (35.3)	57.9 (47.3)	(14.8)
MCM-41(E)	11.0	71.8	17.2	
MCM-41(E) silylated with TRMS	3.1 (2.0)	29.6 (36.8)	67.3 (47.5)	(13.7)

^a Areas in parentheses are the relative areas of the total four peaks which were used for quantitative calculations.

the preparation of MCM-41 as a comparison. For the samples without silylation, three peaks can be observed. According to Maciel et al.,^{21a} the low-intensity peak at -92 ppm corresponds to surface silicon atoms with two siloxane bonds and two silanol groups, i.e., geminal silanol sites, (SiO)₂*Si(OH)₂ (Q²) which may be either single or hydrogen-bonded, and similarly the resonance at -101 ppm is attributed to surface silicon atoms with three siloxane bonds and one silanol group, i.e., isolated silanol sites, (SiO)₃*SiOH (Q³), while the resonance at -110 ppm is ascribed to surface silicon atoms with four siloxane bonds, i.e., (SiO)₄*Si (Q⁴).^{21a} For the two silylated MCM-41 samples, a strong resonance at 14 ppm besides those resonances observed on unsilylated samples, assigned to the silicon atoms of the attached *Si(CH₃)₃ moiety, is observed. Correspondingly, the intensities for the Q² and Q³ silicon resonances are significantly decreased, while the Q⁴ silicon resonance is substantially increased. The intensity redistributions of these silicon sites are thought to be due to the reactions of surface SiOH groups with chlorotrimethylsilane.

The resolution obtained in the spectra is sufficient for accurate curve fittings to provide relative peak intensities corresponding to different silicon nuclei, except for the Q⁴ sites because of the prohibitively long distance between Si deeper in the lattice and surface H atoms. The peak assignments and the relative peak areas after curve fitting the spectra with a series of Gaussian peaks are listed in Table 2. From these relative peak areas, we can calculate the surface SiOH concentrations, α_{OH} , for the corresponding MCM-41 samples before silylation using

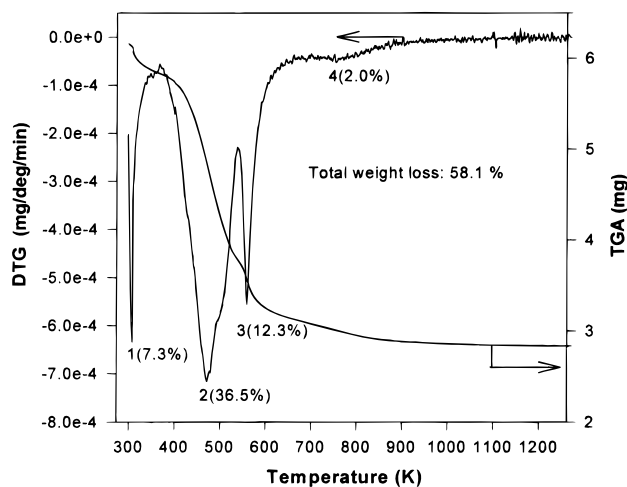
$$\alpha_{\text{OH}} = \frac{S \times (1 + f + f_g^r)}{f} \text{ (number/nm}^2\text{)} \quad (2)$$

where $f = I_s^r / (I_g^r + I_l^r)$, $f_g^r = I_g^r / (I_g^r + I_l^r)$. I_s^r , I_g^r , and I_l^r denote the ^{29}Si peak areas at 14 ppm (attached trimethylsilyl silicon atoms), -92 ppm (unreacted geminal silicon sites), and -101 ppm (unreacted single SiOH sites), respectively; f is the ratio of attached silane silicons to the remaining silanol silicons in modified sample; f_g^r is the fraction of residual geminal silanols in the modified sample; S is the concentration of attached TRMS groups, i.e., the number of chemically bonded TRMS groups per nm² of MCM-41 surface which can be obtained by

$$S = \frac{\Delta W\% \times N_A}{\text{EMW} \times S_{\text{BET}}} \times 10^{-20} \text{ (number/nm}^2\text{)} \quad (3)$$

where $\Delta W\%$ 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). The calculated results are given in Table 3.

TGA Study. Since the concentration of surface SiOH groups in MCM-41 has been found to be related to the heat-treatment temperature,^{2,31} it is necessary to have a clear understanding

**Figure 7.** DTG and TGA curves for the as-synthesized MCM-41 sample.**TABLE 3: Parameters for Calculating Silanol Concentrations in the Two MCM-41 Samples**

sample	S_{BET} (m ² /g)	f_g^r	f	S	W%	α_{OH} (number/ 100 nm ²)
calcined MCM-41	1180	0.0686	0.390	0.668	9.42	2.5
extracted MCM-41	1153	0.0516	0.353	0.754	10.39	3.0

concerning the calcination process. Figure 7 shows the weight loss curves of the as-synthesized MCM-41 sample. Four maxima in the rate of weight loss (peaks 1-4) can be observed. Peak 1, centered at 323 K, is associated with physically adsorbed water, constituting about 7.3% weight loss; peak 2, at about 473 K, related to the decomposition of the template, i.e., the Hoffmann elimination reaction, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+ \rightarrow \text{C}_{16}\text{H}_{32} + \text{N}(\text{CH}_3)_3 + \text{H}^+$, contributes to about 36.5% of the weight loss; peak 3, at 563 K, assigned to the combustion of remaining carbon species (e.g., adsorbed trimethylamine, residual carbon, and deposited carbon), contributes to 12.3% weight loss; and the last peak, peak 4, at about 753 K, which is due to the dehydroxylation of SiOH groups,³⁰ gives a weight loss of about 2.0%.

Discussion

The wall structures of MCM-41 are thought to be amorphous.^{31,32} Therefore, it is not unexpected that the surface chemistry of siliceous MCM-41 is similar to that of silica. All SiOH groups, i.e., single, hydrogen-bonded, and geminal SiOH groups, which could be observed on silica surfaces are also observed on MCM-41 surfaces. However, the number of SiOH groups/nm² over MCM-41 surface is between 2.5 and 3.0, which is far less than that on silica surface (between 5 and 8/nm²). This difference is expected since MCM-41 is better-ordered than silica and therefore a highly condensed surface with less SiOH groups.

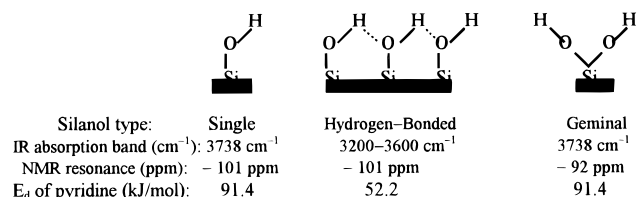


Figure 8. Schematic representation of the three types of SiOH groups in siliceous MCM-41 and their characteristics.

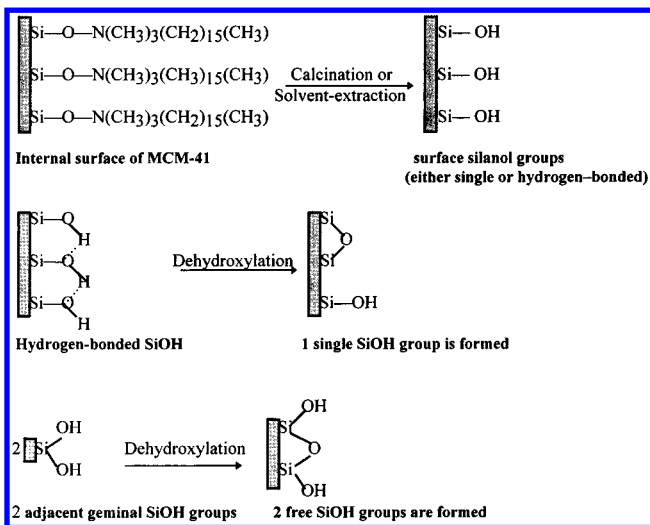


Figure 9. Schematic representation of formation and dehydroxylation processes of SiOH groups in siliceous MCM-41.

The three observed types of SiOH groups have the following characteristics: single SiOH groups with an IR absorption band at 3738 cm^{-1} and magnetic resonance peak at –101 ppm; hydrogen-bonded SiOH groups with an IR absorption band at 3200–3600 cm^{-1} and magnetic resonance peak at –101 ppm; and geminal SiOH groups with an IR absorption band at 3738 cm^{-1} and magnetic resonance peak at – 92 ppm, respectively, as illustrated in Figure 8. The value of the SiOH number, α_{OH} , has contributions from all of these three groups on both the external and internal surfaces. The α_{OH} on our MCM-41 samples is between 2.5 and 3.0, less than that determined by Ishikawa et al.¹⁶ but much more than that determined by Llewellyn et al.¹⁷ We believe that our observations based on NMR method are more reliable since it is further supported by the TGA data shown in Figure 7. From Figure 7, one can know that the total organic content in the as-synthesized MCM-41 is about 53.8% based on anhydrous silica, the stoichiometric molar ratio of Si/N is thus calculated to be 3.79. Therefore, the theoretical silanol number attached to the internal surface is about 2.4/nm² (the internal surface area is 1025 m²/g). Since the internal surface is the dominant surface of MCM-41, the number can be regarded as representing the α_{OH} of MCM-41.

The formation of internal SiOH groups is thought to be related to the formation process of MCM-41 as illustrated in Figure 9, assuming that there are no lattice defects on the internal surface. As can be seen, when one template molecule is removed, one isolated SiOH group is formed. With increasing temperature, dehydroxylation of hydrogen-bonded and geminal SiOH groups take place to form siloxane bonds and simultaneously more free SiOH groups are generated. That is why the intensity of the absorption band at 3738 cm^{-1} increased gradually at higher outgassing temperatures, and the absorption band at 3222 cm^{-1} disappeared (Figure 1). Dehydroxylation of single SiOH groups is considered to be impossible since they are too far apart (0.5 nm)^{21b} and such a process would necessarily involve the

unfavorable formation of highly strained linked structures.³³ Dehydroxylation from geminal groups could also probably be very difficult since silicon does not form siloxane links ($\text{Si}=\text{O}$) readily.³⁴ According to the scheme as proposed in Figure 9, all SiOH groups pendent to the internal surface of MCM-41 should be isolated silanols, including single and hydrogen-bonded SiOH groups; and the geminal SiOH groups come from the external surfaces and/or inside lattice defects. Since the absorption band at 3715 cm^{-1} , which is assigned to vibration of lattice SiOH groups,¹⁸ was not detected in this study (see Figure 1). The geminal groups are believed to be on the external surface. This suggestion may be supported by data presented in Tables 1 and 2. As can be seen, the number of geminal SiOH groups (simulated peak area of Q² sites) is directly proportional to the external surface area of the MCM-41 samples.

The silanol groups cannot be completely replaced by TRMS groups as the absorption band at 3200–3600 cm^{-1} (assigned to hydrogen-bonded SiOH groups) is still observable for the silylated MCM-41 sample (see Figure 2). In addition, since the intensity of absorption for the silylated MCM-41(C) is similar to that of the sample before silylation, the hydrogen-bonded SiOH groups are believed to be not accessible to the silylating agent, chlorotrimethylsilane. Accordingly, the concentration of attached TRMS groups which is about 0.7/nm² (see Table 3) roughly represents the concentration of single SiOH groups since geminal SiOH groups contribute a negligible portion to the concentration of free SiOH groups, and it is unlikely that reaction of two silylating agent can react at a given geminal silanol site because of steric hindrance. The concentration of hydrogen-bonded SiOH groups can then be readily calculated to be 1.8–2.3/nm². The degree of silylation of those SiOH groups on MCM-41 surface can, therefore, be estimated to be about 25%. The TGA results in Figure 7 strongly support the above calculations. The weight loss due to dehydroxylation of hydrogen-bonded SiOH groups is about 1.9%. On the basis of anhydrous silica, the concentration of hydrogen-bonded SiOH groups is about 2.1/nm², which is in good agreement with the NMR results (1.8–2.3).

We postulate that the degree of silylation on MCM-41 surfaces is determined by the concentration of free (i.e., single and geminal) SiOH groups rather than steric considerations as Sindorf et al.²¹ suggested. The effective molecular area of TRMS estimated by assuming that each group occupies a cylindrical volume of space is 0.43 nm². The theoretical maximum concentration of attached TRMS should be, therefore, about 2.5/nm². However, the observed maximum concentration of attached TRMS is only 0.754/nm² in the present study (see Table 3). This is due neither to steric prohibition nor to the lack of SiOH groups (a significant portion of hydrogen-bonded SiOH groups are still on surface). A further study³⁵ confirms this conclusion, when the surface hydrogen-bonded SiOH groups were totally removed and/or transformed to free SiOH groups, the degree of silylation approached 100%. The lack of accessibility of hydrogen-bonded SiOH groups to chlorotrimethylsilane is suggested to be related to the hydrogen bond network which interacts very weakly with organic compounds.³⁶

Conclusion

Three types of SiOH groups are distributed over siliceous MCM-41 surfaces being single, hydrogen-bonded, and geminal SiOH groups with a total density of 2.5–3.0/nm². All these SiOH groups interact strongly with pyridine but with different desorption energies. Hydrogen-bonded SiOH groups can be

substantially removed and/or transformed to isolated SiOH groups by heat treatment. Both single and geminal SiOH groups are highly accessible to silylating agents, such as chlorotrimethylsilane, while hydrogen-bonded SiOH groups seem to be inert to silylating agents due to the stable six-member ring formed between two adjacent SiOH groups. Modified MCM-41 materials by silylation exhibit more hydrophobic surface property and therefore more applicable as adsorbents for the removal of volatile organic compounds in the presence of water vapor.

Acknowledgment. Financial support from the TIL program of the Commonwealth Department of Education, Australia, is gratefully acknowledged. The authors wish to thank Mr. Johann Kwiatowski, the Centre for Magnetic Resonance, The University of Queensland, for his help in NMR measurements.

References and Notes

- (1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, 359, 710.
- (2) Beck, J. S.; Vartuli, 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.
- (3) Kloetstra, R. K.; van Bekkum, H. *J. Chem. Res.* **1995**, 26.
- (4) (a) Corma, A.; Martínez, A.; Martínez-Soria, V.; Montón, J. B. *J. Catal.* **1995**, 153, 25. (b) Corma, A.; Navarro, M. T.; Pariente, J. P. *J. Chem. Soc., Chem. Commun.* **1994**, 147. (c) Corma, A.; Navarro, M. T.; Pérez-Pariente, J.; Sánchez, J. *Stud. Surf. Sci. Catal.* **1994**, 84, 69.
- (5) Sayari, A. *Chem. Mater.* **1996**, 8, 1840.
- (6) (a) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, 368, 321. (b) Tanev, P. T.; Pinnavaia, T. J. In *Access in Nanoporous Materials*; Pinnavaia, T. J., Thorpe, Eds.; Plenum Press: New York, 1995; p 13.
- (7) (a) Branton, P. J.; Hall, P. G.; Sing, K. S. W. *J. Chem. Soc., Chem. Commun.* **1993**, 1257. (b) Branton, P. J.; Hall, P. G.; Sing, K. S. W.; Reichert, H.; Schüth, F.; Unger, K. K. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 2965. (c) Branton, P. J.; Hall, P. G.; Treguer, M.; Sing, K. S. W. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 2041.
- (8) (a) Rathousky, J.; Zukai, A.; Franke, O.; Schulz-Ekloff, G. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 2821. (b) Rathousky, J.; Zukai, A.; Franke, O.; Schulz-Ekloff, G. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 937.
- (9) Ioneva, M. A.; Newnan, G. K.; Harwell, J. H. In *Novel Adsorbents and Their Environmental Applications*; AIChE Symp. Ser. **1995**, 91, 40.
- (10) Wu, C. G.; Bein, T. *Science* **1994**, 266, 1013. (b) Wu, C. G.; Bein, T. *Science* **1994**, 264, 1757. (c) Wu, C. G.; Bein, T. *Chem. Mater.* **1994**, 6, 1109.
- (11) Huber, C.; Moller, K.; Bein, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2619.
- (12) Zhao, X. S.; Lu, G. Q.; Zhu, H. Y. *24th Australia and New Zealand Chemical Engineering Conference and Exhibition* **1996**, 4, 39.
- (13) Pöpl, A.; Baglioni, P.; Kevan, L. *J. Phys. Chem.* **1995**, 99, 14156.
- (14) Chen, J.; Li, Q.; Xu, R.; Xiao, F. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2694.
- (15) McCullen, S. B.; Vartuli, J. C. U.S. Patent 5,156,829, 1992.
- (16) Ishikawa, T.; Matsuda, M.; Yasukawa, A.; Kandori, K.; Inagaki, S.; Fukushima, T.; Kondo, S. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 1985.
- (17) Llewellyn, P. C.; Schüth, F.; Grillet, Y.; Rouquerol, F.; Rouquerol, J.; Unger, K. K. *Langmuir* **1995**, 11, 574.
- (18) Jentys, A.; Pham, N. H.; Vinek, H. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 3287.
- (19) Hill, H. D. W.; Zens, A. P.; Jacobus, J. *J. Am. Chem. Soc.* **1979**, 101, 7090.
- (20) (a) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J. *J. Phys. Chem.* **1985**, 89, 277. (b) Fyfe, C. A.; Lyster, J. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1979**, 101, 1351.
- (21) (a) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, 103, 4263. (b) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1983**, 87, 5516. (c) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, 86, 5208. (d) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, 105, 3767. (e) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, 105, 1487. (f) Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J. Am. Chem. Soc.* **1980**, 102, 7606. (g) Maciel, G. E.; Haw, J. F.; Chuang, I.; Hawkins, B. L. *J. Am. Chem. Soc.* **1983**, 105, 5529.
- (22) Haukka, S.; Lakomaa, E. L.; Root, A. *J. Phys. Chem.* **1993**, 97, 5085.
- (23) (a) Gillis-D'Hamers, I.; Cornelissens, I.; Vrancken, K. C.; Van Der Voort, P.; Vansant, E. F. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 723. (b) Vansant, E. F.; Van Der Voort, P.; Vrancken, K. C.; *Stud. Surf. Sci. Catal.* **1995**, 93, 109.
- (24) (a) Richards, R. E.; Rees, L. V. C. *Zeolites* **1986**, 6, 17. (b) Dima, E.; Rees, L. V. C. *Zeolites* **1987**, 7, 219. (c) Cvetanovic, R. J.; Amenomiya, Y. *Adv. Catal.* **1967**, 17, 103.
- (25) Schrader, G. L.; Cheng, C. P. *J. Phys. Chem.* **1983**, 87, 3675.
- (26) Nikiel, L.; Zerda, T. W. *J. Phys. Chem.* **1991**, 95, 4063.
- (27) Zhao, X. S.; Lu, G. Q.; Millar, G. J.; Li, X. S. *Catal. Lett.* **1996**, 38, 33.
- (28) Zhu, H. Y.; Zhao, X. S.; Lu, G. Q.; Do, D. D. *Langmuir* **1996**, 12, 6513.
- (29) Lu, G. Q.; Do, D. D. *Sep. Technol.* **1992**, 2, 19.
- (30) Basu, P.; Ballinger, T. H.; Yates, Jr., J. T. *Rev. Sci. Instrum.* **1988**, 59, 1321.
- (31) Chen, C. Y.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1993**, 2, 27.
- (32) Feuston, B. P.; Higgins, J. B. *J. Phys. Chem.* **1994**, 98, 4459.
- (33) Peri, J. B.; Hensley, A. L. *J. Phys. Chem.* **1968**, 72, 2926.
- (34) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.
- (35) Zhao, X. S.; Lu, G. Q.; Millar, G. J.; Whittaker, A. K. *International Symposium on Zeolites and Microporous Crystals*, in press.
- (36) Hair, M. C.; Hertl, W. *J. Phys. Chem.* **1969**, 73, 4269.