^{29}Si Solid-State NMR Study of Mesoporous M41S Materials

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^{29}Si NMR T_1 relaxation times of M41S materials have been measured using the saturation recovery pulse sequence and T_{CP} and $T_{1\varrho}$ relaxation times measured using variable contact time ^{29}Si CP NMR. T_1 relaxation times are considerably shorter for Q^3 silicon atoms than Q^4 silicon atoms, and optimum conditions for recording quantitative spectra are reported. On this basis accurate Q^3/Q^4 silicon atom ratios are determined and a modified mechanism of silicate condensation is proposed. Relaxation rates are compared with those of amorphous silica gels.

Introduction

The recent development of mesoporous M41S silicates[1,2] has generated a great deal of interest as they exhibit the most uniform pore size in the range 15–100 Å of any known inorganic structure. The unique synthesis based upon surfactant templating allows the pore size to be easily tuned by altering the surfactant chain length. Furthermore, a whole variety of elements other than silicon may be incorporated into the network[3,4] imparting a range of chemical and physical properties. Finally, the internal hydroxylated surface is amenable to attachment by a plethora of functional groups.[5] Consequently, M41S materials have tremendous potential in the areas of catalysis, separation, waste treatment, and optoelectronics.[6]

Presently detailed structural knowledge of these materials is limited because, although having long-range order, they are noncrystalline. Consequently, diffraction techniques can provide only simple information such as pore repeat distances.[7] ^{29}Si solid-state NMR as a probe for local order is therefore a valuable tool for elucidating local silicate environments. Accurate, quantitative ^{29}Si NMR provides key information for determining chemical composition of the walls and thereby helps to infer the wall structure. For quantitative measurements a sufficient delay must be incorporated into the NMR experiment in order to allow full relaxation and ^{29}Si, as a low-abundant spin-half nucleus, often exhibits extremely long spin–lattice (T_1) relaxation times in silicates.[8] To date many spectra have appeared in the literature with a variety of relaxation times ranging from 8 s to several hundred seconds. To efficiently record quantitative ^{29}Si NMR spectra of M41S materials, we have measured the T_1 relaxation times of all spectral components. The results show that not only are the T_1 relaxation times relatively long but they also differ for silicon atoms in different chemical environments.

To overcome experimental difficulties associated with very long repetition times for recording ^{29}Si NMR spectra, cross-polarization techniques are often employed. These have the advantage that repetition rates are governed by ^{1}H relaxation rather than ^{29}Si relaxation which is usually comparatively short. However, spectra become nonquantitative without a specific knowledge of two other relaxation times, that is, the cross-polarization time (T_{CP}) and the proton spin–lattice relaxation time in the rotating frame ($T_{1\varrho}$). A knowledge of these relaxation times can also provide important additional structural information. Here we report these relaxation times for M41S materials and use the values to infer wall detail and proton mobilities.

Experimental Section

^{29}Si magic-angle spinning (MAS) NMR spectra were recorded on both Varian Unity 300 and Bruker MSL 400 solid-state spectrometers operating at 59.591 and 79.494 MHz. Chemical shifts are referenced to tetramethylsilane (TMS). Samples were spun at 3.5 kHz using double-bearing zirconia rotors. The saturation recovery technique was used to measure T_1 owing to the long spin–lattice relaxation times. In this technique the signal is first saturated by a series of 90° pulses separated by a short period. A time τ is then left for the magnetization to recover before a final 90° read pulse is applied. A typical experiment involves 60 acquisitions at eight different τ values. From the resultant series of spectra the T_1 relaxation times can be calculated. Variable contact time (range 0.2–30 ms) cross-polarization experiments were performed using a recycle delay of 5 s.

M41S materials were synthesized via two different routes. Preparation A involved combining 25 wt % in aqueous cetyl-

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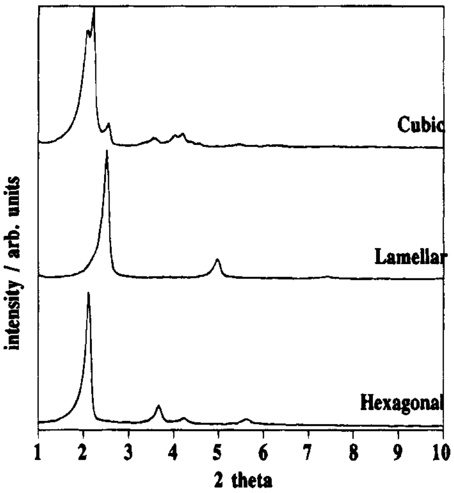

Figure 1. Powder X-ray diffraction patterns of hexagonal, lamellar, and cubic M41S materials used in the ^{29}Si solid-state NMR experiments.

Table 1. Preparation A

	SiO_2	H_2O	CTAC	TBA
hex	0.043	0.820	0.009	0.008
cubic	0.065	1.301	0.013	0.014

Table 2. Preparation B

	SiO_2	H_2O	CTAC	NaOH
hex	0.007	0.783	0.005	0.005
lam	0.009	0.783	0.005	0.005

trimethylammonium chloride (CTAC, Aldrich) with tetrabutylammonium silicate (preparing by combining 40 wt % in water tetrabutylammonium hydroxide (TBAOH, Lancaster) and fumed silica (BDH) in a weight ratio of 10:1). To this were added additional water and fumed silica. Preparation B entailed dissolving sodium hydroxide (Vickers Laboratories Ltd., 97% assay) in water then adding 25 wt % CTAC, 98% tetraethyl orthosilicate (TEOS, Aldrich) and additional water. Molar concentrations for all preparations are given in Tables 1 and 2. All samples were heated at 90 °C for 72 h in Teflon-lined bottles and then washed with copious amounts of water on a Buchner funnel and allowed to dry at ambient temperature. Calcination was carried out at 540 °C for 7 h in flowing air.

Results and Discussion

The materials described in this paper were characterized by powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The XRD patterns are characteristic of M41S mateials[1] and can be seen in Figure 1, and the TGA curves in Figure 2. ^{29}Si MAS NMR spectra for all samples exhibit two partially resolved resonances at −100.7 and −110.3 ppm characteristics of Q^3 and Q^4 silicon environments. Typical values for the individual T_1 relaxation times in various mesoporous materials are given in Table 3.

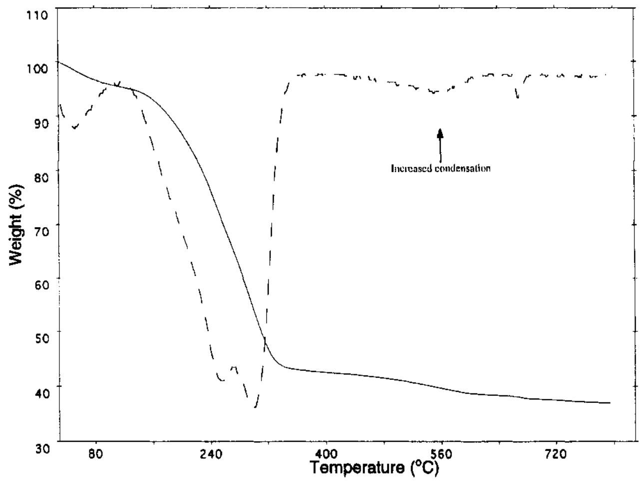

Figure 2. Thermogravimetric analysis curve of a hexagonal as-prepared M41S exhibiting three regions of weight loss: pore water loss room temperature → 100 °C; surfactant loss 130 °C → 300 °C; condensation of Q^3 units 500 °C → 600 °C (solid line weight, dashed line first-derivative weight loss).

Table 3. T_1 Relaxation Times in M41S Materials Calculated Using the Saturation Recovery Technique

sample	T_1 (s) ± 3 s	
	Q^3 peak	Q^4 peak
Si hexagonal calcined	68	125
Si hexagonal uncalcined	52	120
Si cubic uncalcined	64	106
Si lamellar uncalcined	31	69
Si kanemite uncalcined[a]	42	71

[a] M41S preparation using kanemite as SiO_2 source prepared according to ref 9.

Table 4. Q^3/Q^4 Silicon Atom Ratios in M41S Materials

sample	percentage area of peak		
	Q^3 peak	Q^4 peak	Q^3/Q^4
Si hexagonal calcined	23	77	0.30
Si hexagonal uncalcined	37	63	0.59
Si cubic uncalcined	37	63	0.59
Si lamellar uncalcined	49	51	0.96
Si kanemite uncalcined	40	60	0.67

The T_1 relaxation times are moderately long in comparison to other silicate materials which can vary between a few seconds to over 1 h in some amorphous glasses.[8] The Q^4 signals generally relax almost twice as slowly as the Q^3 signals. To achieve quantitatively reliable spectra, full relaxation of all resonances must be allowed. A period of 5 times the longest T_1, i.e., around 600 s delay should be left between pulses. Accurate Q^3/Q^4 ratios determined from deconvolution of spectra recorded under quantitative conditions are given in Table 4. The mechanism for relaxation is not clear. In zeolites the relatively short relaxation times result from coupling to paramagnetic oxygen.[8] Such a mechanism might be operative in M41S materials, although dipolar coupling to mobile protons cannot be ruled out. The marked difference in relaxation times between Q^3 and Q^4 suggest, however, that the Q^3 silicon atoms are closer to the relaxation source which is consistent with the view that Q^3 silicon atoms line the M41S pores.

The Q^3/Q^4 ratios provide important information regarding the structure and mechanism of formation of the silicate walls. First, there is a substantial difference in the Q^3/Q^4 ratio between layered M41S materials and the other M41S materials. Note that upon calcination of the hexagonal material the Q^3/Q^4 ratio is reduced, indicating increased condensation of the silicate structure. This also exhibits itself as a weight loss at temperatures in excess of 500 °C in TGA analysis (Figure 2). Assuming that Q^3 silicon atoms reside at the pore surface this suggests that lamellar materials

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Table 5. $T_{1\varrho}$ and T_{CP} Relaxation Times in M41S Materials Derived Using Variable Contact Time ^{29}Si NMR Cross-Polarization Experiments

	Q^3 silicon atoms		Q^4 silicon atoms	
sample	^{1}H $T_{1\varrho}$ (ms)	T_{CP} (ms)	^{1}H $T_{1\varrho}$ (ms)	T_{CP} (ms)
Si hex calcined rehydrated	40.4	2.9	>400	5.0
Si hex calcined dehydrated[a]	>400	>20	>400	>20
Si hex uncal	9.0	1.3	18	2.1
Si lam uncal	9.0	1.5	26	2.0
Si cubic uncal	5.0	1.0	15	2.0
Si/Al Hex uncal	10.7	1.2	25	2.0

[a] Dehydrated at 250 °C and 10^{-3} Torr for 2 days.

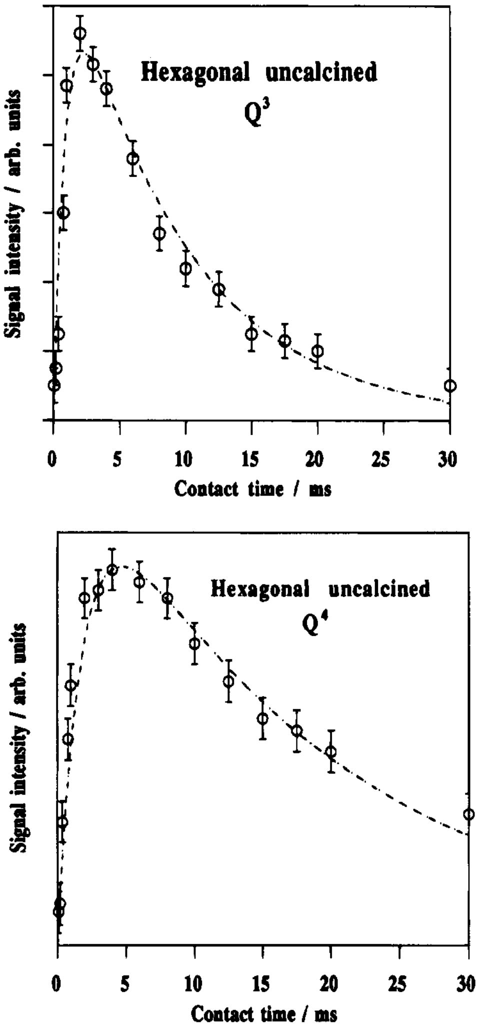

Figure 3. Theoretical fit for variable contact time cross-polarization spectra of uncalcined hexagonal M41S. Magnetisation increase is due to transfer of polarization from ^{1}H to ^{29}Si (time constant T_{CP}) and magnetization decay is due to ^{1}H spin-locked relaxation (time constant $T_{1\varrho}$).

have thinner walls. Indeed the Q^3/Q^4 ratio of ca. 1 suggests a wall composed of two Q^4 layers bordered by one Q^3 layer. Evidence complimentary to the T_1 measurements can be derived from variable contact time CP experiments, the results from which can be seen in Table 5. Data from one such experiment along with exponential fits can be seen in Figure 3.

The response of the Q^3 and Q^4 silicon atoms in the uncalcined hexagonal siliceous materials to CP conditions are very different (Table 5). The T_{CP} of the Q^3 silicon atoms is short (1.3 ms), and as the dipolar nature of this interaction is distance related this suggests an interaction of a silicon atom with protons in close proximity. The $T_{1\varrho}$ relaxation is known to result from fluctuations in the magnetic field of protons due to their motion. The reasonably small value of 9 ms for the $T_{1\varrho}$ of the protons interacting with the Q^3 atoms provide evidence that these protons are fairly mobile. The Q^4 silicon atoms have a slower T_{CP} of 2.1 ms and interact with protons with a $T_{1\varrho}$ of 18 ms. The slower T_{CP} of Q^4 silicons implies that they are further from a proton source than are Q^3 atoms, and the slower $T_{1\varrho}$ indicates that these protons are less mobile. Thus a picture emerges with Q^4 silicon atoms found embedded in the walls of M41S materials interacting with less mobile protons close to the pore surface and Q^3 atoms located on the outer edge of the walls able to interact with more mobile protons found in central positions of the channels. This is shown schematically in Figure 4. It cannot be ruled out that the silanol groups also exist within the body of the walls.

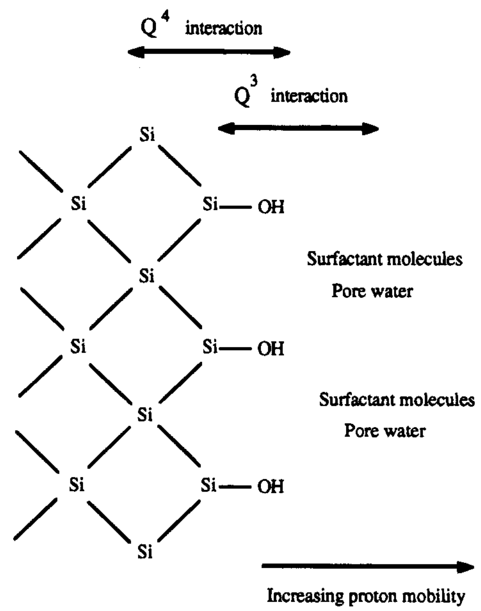

Figure 4. Schematic representation of CP interactions in M41S materials showing how Q^3 silicon atoms will be in dipolar contact with more mobile protons which are located away from the pore walls and Q^4 silicons in contact with more rigid protons located near the pore wall.

Marked differences exist in the responses of calcined and uncalcined hexagonal siliceous materials. First, T_{CP} times for both types of silicon atom in calcined materials are slower than in uncalcined ones, though relatively Q^3 atoms still have a faster T_{CP} time than Q^4 atoms within calcined materials. This suggests that within calcined materials Q^4 atoms are still more distant from the proton source, although compared with uncalcined materials the proton pool available for cross-polarization has been reduced by calcination, which has resulted in longer time constants. Clearly the surfactant template molecules present in uncalcined samples, chemical analysis showing carbon is 38.9% of the as-prepared product, offer a more abundant source of protons for cross-polarization than does pore water in rehydrated calcined samples. A similar relationship exists for proton $T_{1\varrho}$ times affecting Q^3 and Q^4 silicon atoms. Proton interacting with Q^4 silicons have longer $T_{1\varrho}$ times than those interacting with Q^3 silicons, though calcination has reduced both values in comparison with the uncalcined material. Again this indicates that the proton source responsible for the cross-polarization of the Q^4 atoms is less mobile than that affecting Q^3 silicon atoms. This suggests that water molecules that occupy the channels of these mateials, following calcination and rehydration, are less mobile than surfactant template molecules removed and that these water molecules have very limited mobility when in close proximity to pore walls.

Data from a dehydrated hexagonal M41S material is also reported. This material was dried on a vacuum line and then sealed in a zirconium rotor within a nitrogen-filled glovebox. To exclude moisture from the sample during the experiment, nitrogen was employed as the drive and bearing gas for magic-angle rotation. Absolute figures for T_{CP} and $T_{1\varrho}$ are difficult to determine because of increasing signal intensity after contact times of 30 ms. The long $T_{1\varrho}$ times reflect a lack of mobility in the protons providing the magnetisation for cross-polarization, i.e., hydroxyl protons attached to the Q^3 silicon atoms, other proton sources having been removed. This is confirmed by ^1H MAS NMR of a dehydrated calcined M41S material (Figure 5). A single signal at 2 ppm is observed, which is attributed to the hydroxyl protons attached to the Q^3 silicons. More importantly, T_{CP} times are long, suggesting a weak dipolar interaction with these protons, much weaker than in other samples. This indicates that the hydroxyl protons of the Q^3 silicon atoms are not the main source of proton magnetization for CP in M41S materials but rather pore water and surfactant template molecules for calcined and uncalcined samples, respectively.

It is interesting to compare ^{29}Si relaxation time constants for M41S materials with values for amorphous silica gels.[10-12] For a range of materials (see Table 6) the T_{CP} and $T_{1\varrho}$ values are similar for the two systems; however, the T_1 is considerably shorter for the amorphous silica gels. This suggests that the detailed structure of M41S is different to that of an amorphous silica gel.

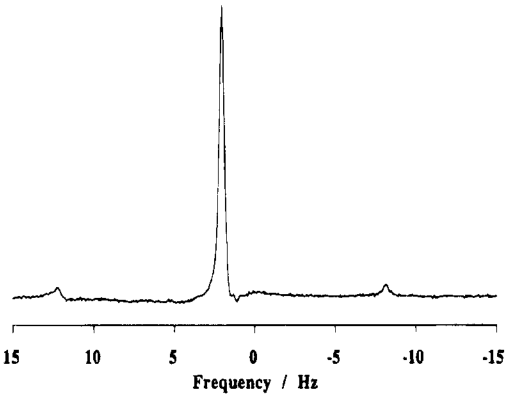

Figure 5. ^1H MAS NMR spectrum of a dehydrated calcined M41S material recorded on a Bruker 400 MSL solid-state spectrometer operating at 400.13 MHz, using a Chemagnetics multinuclear Pencil probe. A Hahn echo with a 5 s repetition time was used to record the FID, and the resultant signal referenced to TMS.

Table 6. Comparison of Relaxation Times between M41S and Amorphous Silica Gel

		amorphous silica gel[10-12]	M41S
T_1 (s)	Q^3	10–40	30–70
	Q^4	20–50	70–125
T_{CP} (ms)	Q^3	1–3	1–3
	Q^4	2–15	2–5
$T_{1\varrho}$ (ms)	Q^3	15–25	5–40
	Q^4	15–30	15 to >400

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