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Structural characterization of organically-modified porous silicates synthesized using CTA$^+$ surfactant and acidic conditions†

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Organically-modified silicates have been synthesized from $RSi(OEt)_3$ (R=CH_3, C_2H_5, C_8H_{17}, CH_2=CH or C_6H_5) and TEOS under acidic conditions, in the presence of cetyltrimethylammonium bromide (CTAB). The introduction of $RSiO_{1.5}$ units with R/Si=0.2:1, prevents the system from adopting a high degree of hexagonal mesostructural order, except when R=C_6H_5. For the sample containing the phenyl functionality, removal of the surfactant by calcination at 350 °C appears to be more complete, and less disruptive to mesoscopic ordering than solvent extraction using EtOH. Nitrogen adsorption measurements on the hexagonally ordered calcined sample that still contains phenyl groups, yields a type I isotherm, typical of a microporous solid with a pore size distribution centered at 15 Å.

Introduction

The discovery of the MCM series of mesoporous silica-based materials has opened the way to entirely new mesostructured materials.[1] Many applications, such as adsorption, ion exchange, catalysis, and sensing, require materials with specific surface properties.[2] Organic functions can be introduced at the silica surface, by two methods. One is based on the covalent grafting of organic entities at the surface of the mesoporous silica substrate, *via* the use of organically modified trialkoxysilanes, $RSi(OR')_3$. This has been used to graft Mn^{III} Schiff base complexes for catalytic applications[3] or thiol functions for environmental applications.[4] Another possibility for the introduction of organic functions is a one-pot synthetic approach, based on co-condensation reactions of tetraethoxysilane (TEOS) and $RSi(OR')_3$, in the presence of a surfactant solution. Several short communications have recently reported on the preparation of such organically modified MCM-type materials. Octyl chains and phenyl groups have been introduced,[5] as well as less inert groups such as amino,[6–8] vinyl,[9] cyano groups[7] and thiol, epoxy, allyl, and imidazolyl functions.[6,10] The experimental conditions were mainly those used for the synthesis of MCM-41 such as basic conditions and the use of cetyltrimethyl ammonium bromide (CTAB) as the surfactant ($0.12 \leqslant$ CTAB/Si $\leqslant 0.15$). An alternative neutral templating approach using dodecylamine as the surfactant, already developed for pure mesoporous silicates by Tavev and Pinnavaia,[11] was also used in the case of the amino, cyano and imidazolyl derivatives.

Under basic conditions, Mann and co-workers[5] reported that they were unable to obtain hexagonally ordered materials using 10 mol% octyltriethoxysilane, and that surfactant extraction disrupted the structure. However, trialkoxysilanes modified with alkyl groups are known to present a higher reactivity towards hydrolysis under acidic conditions.[12] This prompted us to investigate the preparation of organically-modified mesoporous silicates, under acidic conditions, using various (alkyl or aryl)triethoxysilanes, $RSi(OEt)_3$ [R = CH_3 (MTES), C_2H_5 (ETES), C_8H_{17} (OTES), CH_2 = CH (VTES) or Ph (PhTES)] and TEOS as hybrid precursors. The experimental conditions were adapted from a procedure developed by Stucky and co-workers for the synthesis of hexagonal SBA-3, using HCl and CTAB as the structure directing agents.[13] The influence of the organic functions on the extent of mesoscopic order obtained in the as-synthesized samples has been investigated, and the samples prepared with $PhSi(OEt)_3$ have been more specifically characterized.

Experimental section

All the samples, labeled X1T4, were prepared as follows: the two alkoxides, TEOS and XTES (X = M, E, O, V or Ph), were pre-hydrolyzed in a 4 : 1 molar ratio for 1 h at room temperature in ethanol [EtOH/Si = 4 : 1; H_2O/Si = 1 : 1; pH (HCl) = 1.2] to initiate co-condensation reactions between the precursors[14] and to prevent phase separation. This solution was then mixed with an acidic solution of CTAB (CTAB/Si = 0.12 : 1; HCl/H_2O/Si = 9.2 : 130 : 1) and stirred for 2 h. The precipitate was then filtered, rinsed with distilled water and dried at 100 °C. Surfactant extraction was performed by stirring a suspension of the solid product in EtOH at 60 °C for 2 h (50 ml EtOH per g of sample). The extracted material was filtered, washed with EtOH and air-dried at 100 °C.

The low angle X-ray diffraction patterns were recorded at LURE, the French synchrotron facility, with a wavelength of $\lambda = 1.2836$ Å. The elemental analyses were done by the 'Laboratoire Central d'Analyse du CNRS' at Vernaison (France). The ^{29}Si and ^{13}C MAS-NMR spectra were recorded on a MSL300 Bruker spectrometer at 59.6 and 75.47 MHz respectively, with 4-kHz spinning rates. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP 2010 surface analyzer. Samples were degassed at 60 °C under 3 μm Hg pressure.

Results

Influence of the R group

The ^{29}Si MAS-NMR spectra recorded on all of the X1T4 samples show that the two types of Si units have been incorporated into the crosslinked silica network. Quantitative analyses reveal a T/Q molar ratio equal to the one used for the synthesis for Ph1T4 (20 : 80), slightly higher for M1T4 (24 : 76), E1T4 (24 : 76) and O1T4 (26 : 74), and much higher for V1T4 (40 : 60). Elemental analyses (Table 1) shows that the CTAB/Si molar ratio present in each of the as-synthesized samples is slightly higher compared to the initial ratio (0.12 : 1). Interestingly, the analyses reveal that the Cl/Si molar ratio

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Table 1 Results of elemental analysis and ^{29}Si NMR on selected samples

Sample	Elemental analysis					^{29}Si NMR
	C/Si	H/Si	N/Si	Cl/Si	Br/Si	T/Q ratio
M1T4	3.03	7.93	0.14	0.15	0.006	24:76
O1T4	5.52	13.50	0.17	0.17	0.008	26:74
Ph1T4	4.59	9.17	0.17	0.17	0.009	20:80

Table 2 d_{100} distance extracted from the X-ray diffraction patterns

Sample	d_{100}/Å
M1T4	36.5
E1T4	34.0
O1T4	39.2
V1T4	32.0
Ph1T4	34.4

matches the N/Si ratio, suggesting that the charge of the cationic surfactant (S^+) is entirely counter-balanced by chlorine anions, the amount of bromine being negligible. A similar result was already published for a SBA-3 sample prepared only using TEOS as the silicate source.[15] We can therefore consider that the ion pairs S^+Cl^- engage in weak interactions with a neutral organically-modified silicate framework.

The X-ray diffraction patterns of these samples (Fig. 1) show that the presence of $RSiO_{1.5}$ units strongly influences the degree of ordering of the SBA-3 type network. For $R = CH_3$, C_2H_5 and $CH{=}CH_2$ only rather broad (100) peaks are present which indicate poor degrees of ordering. The sample with $R = C_8H_{17}$ also shows only one peak but with higher intensity, which reflects better mesoscopic organization; but the most ordered sample is the one prepared with PhTES: a sharp (100) peak is present with two additional (200) and (110) peaks. This pattern is clearly due to a two-dimensional hexagonal phase.[13] This relatively high degree of ordering could reflect specific interactions between the Ph groups and the surfactant chains.

The presence of R groups not only influences the degree of network ordering, but also the ordering lengthscale as evident in Table 2 through the change in the d_{100} spacing depending on R.

Characterization of the sample prepared from PhTES and TEOS (Ph1T4)

The most ordered sample (Ph1T4) has been subjected to surfactant extraction. Two methods were tested: controlled calcination and solvent extraction using ethanol. Calcination was performed at 350 °C for 1 h in air. The temperature was chosen according to TG results which showed first a weight loss between 200 and 350 °C (36%), followed by a second one between 450 and 600 °C (19%). According to the chemical analysis results, the surfactant extraction is expected to produce a 40% total weight loss which is in good agreement with the first observed weight loss, considering that condensation of the silicate network will occur simultaneously, causing additional weight changes. Decomposition of the phenyl groups are expected to cause a 16% weight loss, once again in good agreement with the second observed weight loss. The surfactant species can thus be removed by controlled calcination at 350 °C, without decomposition of the phenyl groups.

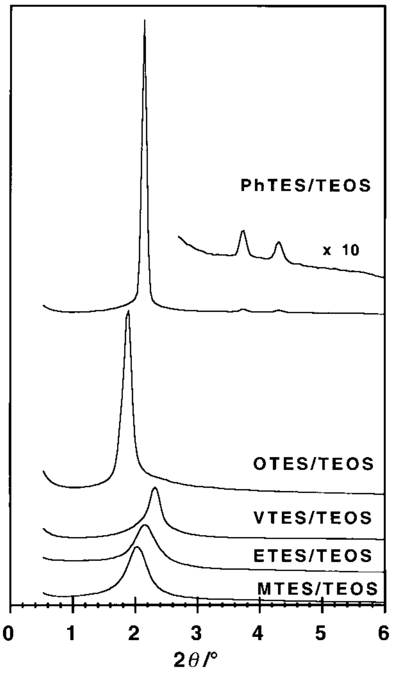

Fig. 1 X-Ray diffraction patterns of various as-synthesized samples.

This procedure can be used for this sample only because of the high thermal stability of the Si–Ph bond under an oxidative environment but cannot be used when R is an alkyl chain. In those cases, a simple solvent extraction procedure in pure ethanol, developed for the MCM-type samples prepared with a non-ionic surfactant, can be used[11] because of the weak interactions that exist in our samples between the silicate framework and the S^+Cl^- pair. There is no need to use an acid–solvent extraction method like the one used for similar materials prepared under basic conditions,[5] and for which strong electrostatic interactions exist between the cationic surfactant head group and the negatively charged silicate surface. The X-ray diffraction pattern of the Ph1T4 samples, obtained after surfactant extraction (Fig. 2) shows that the calcined material retained its high level of mesoscopic ordering with a slight contraction of the hexagonal cell parameter, from 39.5 Å in the as-synthesized Ph1T4 to 35.4 Å in the calcined Ph1T4 sample. Conversely, the solvent extraction with ethanol leads to a disruption of the mesoscopic ordering, as evidenced by the presence of a single weak (100) peak at $d = 26.2$ Å.

The efficiency of the surfactant extraction procedure can be characterized by ^{13}C CP-MAS NMR (Fig. 3): the spectrum

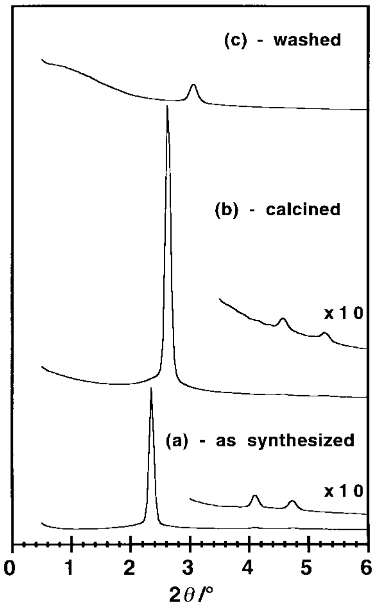

Fig. 2 X-Ray diffraction patterns of Ph1T4 samples, after surfactant extraction.

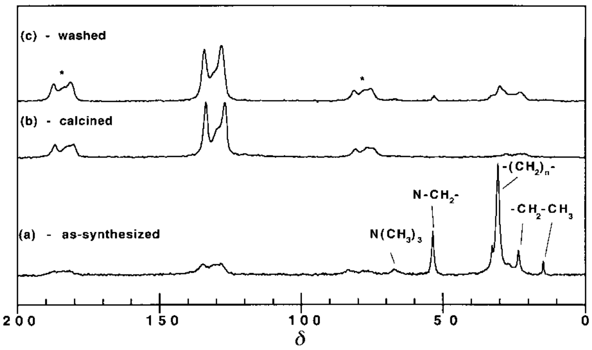

Fig. 3 ^{13}C CP MAS NMR spectra of as-synthesized Ph1T4 (a), and after surfactant extraction *via* calcination (b) or washing in ethanol (c).

of the as-synthesized sample shows the characteristic peaks of the phenyl groups at δ 128 and 134 as well as those due to the surfactant chains. The ^{13}C CP-MAS spectrum of the calcined sample shows no evidence of peaks due to the surfactant chains, while some residual peaks are still present in the spectrum of the EtOH-washed sample. The organically-modified silicate networks have been characterized by ^{29}Si MAS-NMR spectra (Fig. 4) and the results are summarized in Table 3. The as-synthesized sample shows a degree of condensation of 88% for both T and Q units. Calcination, as well as solvent extraction, leads to more condensed networks, 95% and 93%, respectively for the degrees of network condensation.

The analyses of the adsorption–desorption isotherms measured on various surfactant extracted samples are summarized in Table 4. Unlike the sample prepared with pure TEOS which exhibits a type IV isotherm, characteristic of a mesoporous solid, the three samples prepared from PhTES and TEOS present a type I isotherm, typical of microporous solids (Fig. 5). This is in perfect agreement with data reported on similar materials prepared under basic conditions.[16] The same authors have also shown that a type IV isotherm can be obtained for phenyl modified MCM-41 samples if mesitylene, used as a swelling agent, is introduced during the synthesis.[17] The calcined Ph1T4 sample has a larger pore volume (0.50 cm^3 g^{-1}) compared to the EtOH-washed sample (0.25 cm^3 g^{-1}). This has to be related to a lower degree of ordering for the washed sample, but also to the presence of residual surfactant chains, as shown by ^{13}C MAS-NMR. This sample was then calcined to totally remove the surfactant: the treatment does not improve the degree of network ordering, as seen from the X-ray diffraction pattern, but leads to a slight increase of the pore volume (0.32 cm^3 g^{-1}).

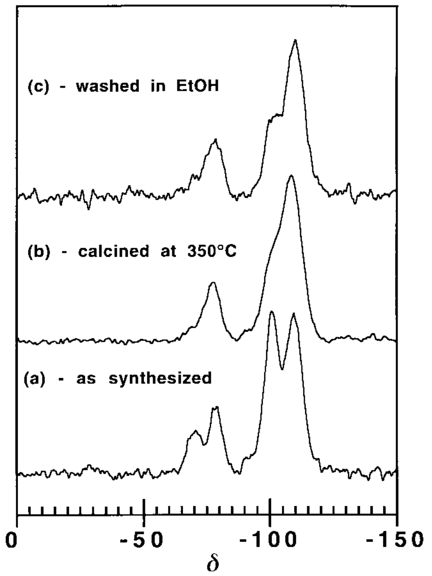

Fig. 4 ^{29}Si MAS NMR spectra of as-synthesized Ph1T4 (a), and after surfactant extraction (b) and (c).

Table 3 Results from ^{29}Si MAS-NMR spectra recorded on the Ph1T4 samples

	% Si units				
Sample	T$_2$	T$_3$	Q$_2$	Q$_3$	Q$_4$
As-synthesized	7	13	5	27	48
Calcined	4	14	0	25	57
Washed	7	15	0	19	59

Table 4 Results from the N$_2$ adsorption–desorption isotherms measured on the Ph1T4 samples after surfactant extraction (results obtained on a sample prepared with TEOS with the same experimental procedure, and calcined at 600 °C are given for comparison)

Sample	Type of isotherm (pore diameter/Å)	S_a^*/m^2 g^{-1}	V_P^*/cm^3 g^{-1}
From TEOS calcined at 600 °C	IV (24 Å)	1010	0.82
Ph1T4 calcined at 350 °C	I (16 Å)	1010	0.50
Ph1T4 washed in EtOH	I (13 Å)	490	0.25
Ph1T4 washed in EtOH, then calcined	I (14 Å)	610	0.32

*S_a: apparent BET surface area; V_P: pore volume.

Conclusions

This paper reports on the preparation of hybrid organic–inorganic silicates obtained under acidic conditions by co-hydrolyzing TEOS and RSi(OEt)$_3$ (R=CH$_3$, C$_2$H$_5$, C$_8$H$_{17}$, CH$_2$=CH or Ph) in the presence of CTAB. The extent of mesoscopic order depends on the nature of the R group, as already mentioned in the literature for preparations done under basic conditions.[5] The (110) and (200) reflection peaks, characteristic of a well-ordered hexagonal phase, could only be seen for the sample containing 20 mole% of PhSiO$_{1.5}$ units. These differences could be due to specific interactions between the phenyl groups and the surfactant chains, which are under investigation.

One major difference with the organically-modified MCM41

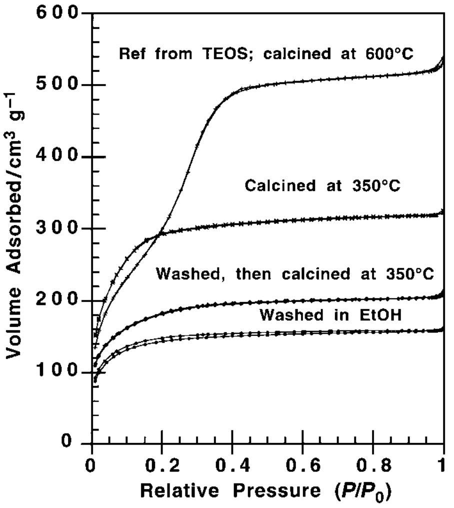

Fig. 5 N$_2$ adsorption–desorption isotherms for two calcined samples prepared from TEOS and PhTES/TEOS.

samples prepared under basic conditions, is the type of interaction between the surfactant and the silicate surface: in the samples prepared under acidic conditions, weak interactions exist between the S^+Cl^- pair and the neutral organically modified silicate framework. This is of great importance regarding surfactant extraction methods, a simple solvent extraction using pure ethanol is possible, and allows easy recycling of the surfactant.

Phenyl containing samples were subjected to surfactant extraction. The hexagonal ordering could be retained after controlled calcination at 350 °C which maintained the phenyl groups intact, while the solvent extraction technique leads to a strong disordering of the structure, as already reported for similar systems in the literature.[6] As a consequence, the porous structures are also different with higher pore volume for the calcined sample. However, the calcination can only be applied for specific systems in which the Si–C bonds are strong enough to sustain such heat treatment.

The exact location of the phenyl groups in the sample still remains obscure. The type of N_2 adsorption–desorption isotherm is characteristic of microporous solids, with a pore diameter of *ca.* 15 Å, smaller than that found in an equivalent sample prepared from pure TEOS (24 Å), which is clearly mesoporous; however, both solid networks have very similar cell parameters, 38 Å for the calcined TEOS-derived sample and 35 Å for the calcined Ph1T4 sample. This strongly suggests that the reduction of the pore size, which does not affect the network geometry, could be related to the presence of the phenyl groups hanging in the pores. Further work is under way to locate the phenyl groups.

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