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Porous silica and polysilsesquioxane with covalently linked phosphonates and phosphonic acids

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In this paper we report on synthesis and characterisation of the first phosphonate and phosphonic acid-modified porous silicas and polysilsesquioxanes. The organosilicon phosphonates $[(EtO)_3Si(CH_2)_3PO(OEt)_2]$ **1** and $[(EtO)_3Si(CH_2)_2PO(OEt)_2]$ **2** have been used to introduce phosphonate and phosphonic acid functionalities to silica and a polysilsesquioxane. Compounds **1** and **2** have been fully characterised (^{1}H, ^{29}Si, ^{31}P and ^{13}C NMR and elemental analysis). Xerogels [from tetraethylorthosilicate (TEOS) or 1,4-bis(triethoxysilyl)benzene (BTESB), and **1** or **2**] bearing functionality of the type $[O_{n/2}(EtO)_{3-n}Si(CH_2)_mPO(OEt)_2]$ and, after treatment with concentrated HCl, functionality of the type $[O_{n/2}(EtO)_{3-n}Si(CH_2)_mPO(OH)_2]$, ($n$ can be 0–2, $m = 2$ or 3) were synthesised and characterised using solid state ^{29}Si, ^{31}P and ^{13}C NMR spectroscopy, elemental analyses and porosimetry measurements. High surface area mesoporous phosphonic acid-modified silicas with a narrow pore size distribution are described.

Introduction

A number of recent reviews have described a growing range of organically modified porous silicas.[1,2] A wide range of organic functions have been introduced and may facilitate various heterogeneous catalytic transformations, including oxidation and carbon–carbon bond formation. We are investigating several different approaches to unprecedented phosphonate/phosphonic acid-modified silicas, including co-polymerisation and grafting techniques involving precursors such as $[(EtO)_3Si(CH_2)_3PO(OEt)_2]$ **1** and $[(EtO)_3Si(CH_2)_2PO(OEt)_2]$ **2**. The extensive work of Clearfield and others[3] on metal phosphonates from the phosphonic acids $RPO(OH)_2$ or diacids $R\{PO(OH)_2\}_2$ illustrates the potential of materials with this type of functionality for applications as sorbents and ion exchangers, and as hosts for intercalation chemistry.

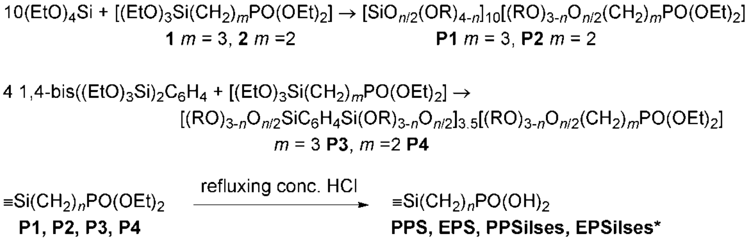
We report here on the first phosphonate/phosphonic acid-modified silica materials obtained using co-polymerisation of suitable precursors by sol–gel methods as illustrated in Scheme 1 below.

Synthesis and characterisation of new materials

Precursors

A previously described route[4] to the precursor compounds $[(EtO)_3Si(CH_2)_3PO(OEt)_2]$ **1** and $[(EtO)_3Si(CH_2)_2PO(OEt)_2]$ **2**, involving radical-promoted addition of $HPO(OEt)_2$ to appropriate allyl or vinyl silicon precursors was followed in this work. Spectroscopic data (solution phase ^{1}H, ^{29}Si, ^{31}P and ^{13}C NMR) for these compounds was not previously reported and is included in this work. The NMR data and assignments for **1** and **2** are given in the experimental section and are consistent with the expected composition (DEPT spectra were recorded to confirm the ^{13}C NMR assignments). In particular, for both **1** and **2**, coupling is evident between some of the CH_2 groups and phosphorus in $[(EtO)_3Si(\mathbf{CH_2})_nPO(\mathbf{OCH_2}CH_3)_2]$ in both the ^{1}H and ^{13}C NMR spectra and for $n = 2$, $^3J_{PSi}$ coupling (45 Hz) is evident from the ^{29}Si NMR spectra. The ^{1}H NMR spectra indicate that each of the methylene protons in $-PO(\mathbf{OCH_2}CH_3)_2$ are uniquely split by phosphorus to give a pair of overlapping 1 : 4 : 6 : 4 : 1 quintets ($^3J_{PH}$ 10 Hz) but are magnetically equivalent in terms of coupling to the neighbouring CH_3 groups for which a simple 1 : 2 : 1 triplet is observed.

The splitting patterns for the CH_2 groups in the bridge between phosphorus and silicon in the compounds $[(EtO)_3Si(\mathbf{CH_2})_nPO(OCH_2CH_3)_2]$ indicate that these protons are magnetically distinct [*e.g.* compound **2** exhibits an AA′BB′P pattern ($^2J_{PH}$ 18 Hz, $^3J_{PH}$ 10 Hz) for each of the bridging CH_2 groups]. This feature suggests that there is some restricted rotation about the C–C bonds between the Si and P in **1** and **2**. We have also developed alternative routes to **1** and **2** using Arbusov chemistry and are currently carrying out further



Scheme 1 PPS (propylphosphonic acid-modified silica), EPS (ethylphosphonic acid-modified silica), PPSilses (propylphosphonic acid-modified silsesquioxane), EPSilses (ethylphosphonic acid-modified silsesquioxane).

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investigations into the radical reaction leading to compounds **1** and **2** discussed above. This latter work will be reported elsewhere. The focus of this paper is the novel phosphonic acid-modified silicas derived from these precursors.

Synthesis and characterisation of the first examples of phosphonato and phosphonic acid-modified silicas from TEOS and 1 or 2

The reagents TEOS [tetraethylorthosilicate, $(EtO)_4Si$] and $[(EtO)_3Si(CH_2)_3PO(OEt)_2]$ **1** or $[(EtO)_3Si(CH_2)_2PO(OEt)_2]$ **2** were co-polymerised by sol–gel processing in ethanol using dilute acid catalysis and an excess of water, as illustrated in Scheme 1. An initial experiment with TEOS, and compounds **1** or **2** (molar ratio 4 : 1) resulted in phase separation to give a transparent glassy material along with an opaque phase (both amorphous by XRD; see experimental section). Homogeneous monolithic transparent xerogel glasses P1 and P2 were, however, formed when the ratio of TEOS : **1** or **2** was increased to 10 : 1. The solid state CP MAS ^{29}Si,† ^{31}P and ^{13}C NMR for P1 are shown in Fig. 1 and spectroscopic data for both P1 and P2 collated in Table 1. These confirm the presence of the phosphonate group in the silica matrix. In both cases, porous materials P1 ($S = 453\ m^2\ g^{-1}$) and P2 ($S = 143\ m^2\ g^{-1}$) were obtained.

Treatment of powdered P1 and P2 with refluxing concentrated HCl resulted in conversion of the phosphonate ester to the corresponding propylphosphonic acid and ethylphosphonic acid-modified silicas, PPS, and EPS. The solid state ^{29}Si, ^{31}P and ^{13}C NMR spectra for PPS shown in Fig. 2 and the NMR data for PPS and EPS collated in Table 1 confirm the transformation from ester to acid.

Solid state NMR studies

NMR spectroscopic data for P1, P2, PPS and EPS are summarised in Table 1 and assignments are discussed below.

The ^{29}Si data for the co-polymerised materials P1 and P2 containing the phosphonate ester groups have resonances consistent with T environments and Q environments in the ratio T/Q = 0.1, as expected. In comparison with **1**, the ^{13}C NMR resonances from P1 due to the ester groups in $-SiCH_2CH_2CH_2PO(OCH_2CH_3)_2$ and any residual silyl ester occur around δ 16(broad) and 63. The broad resonance around 16 ppm masks the carbon environments α and β to silicon ($-Si\mathit{C}H_2\mathit{C}H_2CH_2P-$), while the carbon α to phosphorus [$-Si(CH_2)_2\mathit{C}H_2P-$] appears at 27 ppm, as in **1**.

In comparison with **2**, the ^{13}C NMR spectrum of P2 has a peak close to δ 5 which we assign to the carbon α to silicon in $-Si\mathit{C}H_2CH_2P-$; the broad resonances at 16 and 63 ppm represent the phosphonate ester and residual silyl ester groups. The resonance at 16 ppm also masks the carbon α to phosphorus in the fragment $-SiCH_2\mathit{C}H_2P-$.

There are two phosphorus resonances present in the ^{31}P spectra of P1 and P2 at around 23 and 34 ppm. The resonance at *ca.* 34 ppm is close to that in the precursor compounds **1** and **2**. The much lower intensity resonance at *ca.* 23 ppm is discussed further below.

The products PPS and EPS, from concentrated HCl treatment of P1 and P2, display T and Q ^{29}Si resonances in the ratio T/Q = 0.1, which indicates that there was no Si–C bond cleavage (further discussion below). In the ^{13}C spectra of both PPS and EPS, the apparent absence of resonances close to 63 ppm due to ester group methylene carbons [$PO(O\mathit{C}H_2CH_3)_2$] (and any residual silyl ester) (see Fig. 2) indicates that hydrolysis of the phosphonate ester was complete. The measured C : P ratios for these samples,

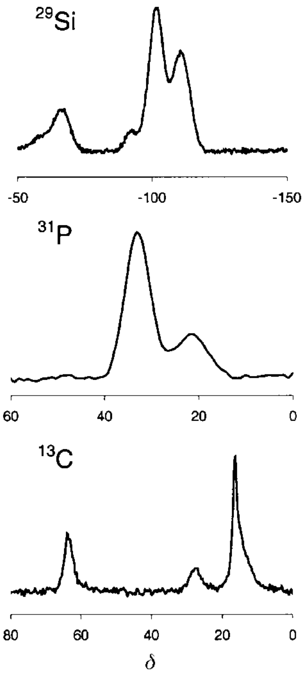

Fig. 1 Solid state ^{29}Si, ^{31}P and ^{13}C NMR for P1.

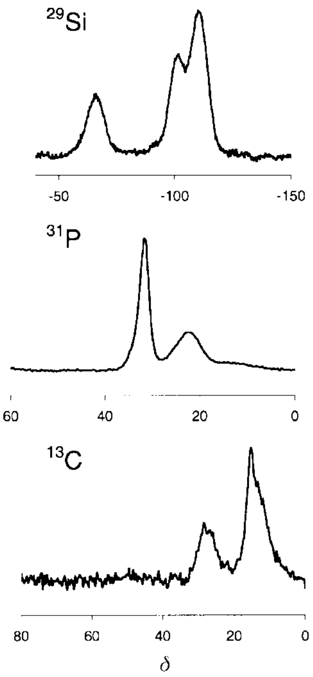

Fig. 2 Solid state ^{29}Si, ^{31}P and ^{13}C NMR spectra for PPS.

Table 1 Solid state NMR spectroscopic data for P1, P2, PPS and EPS

NMR		P1	P2	PPS	EPS
^{29}Si CP MAS	T^1	−57.0	−61.5		—
	T^2	−66.9	−66.9	−65.7	66.9
	Q^2	−90.4	−91.8		
	Q^3	−100.9	−100.8	−101.5	−102.1
	Q^4	−109.7		−110.6	−110.8
^{31}P CP MAS		22.8	24.8 (trace)	22.8	22.8
		34.2	35.3	31.9	32.3
^{13}C CP MAS		16.4	4.7	16.1	4.8
		27.7	16.2	28.9	18.9
		63.8	63.7		

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† ^{29}Si spectra were also measured using SPE (single pulse excitation) MAS (see Fig. 5 and related discussion).

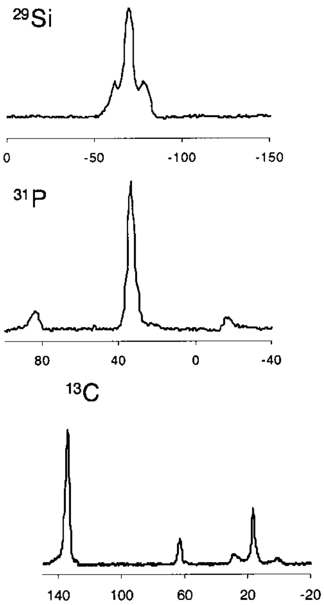

Fig. 3 Solid state ^{29}Si, ^{31}P and ^{13}C NMR spectra for P3.

however, are consistent with a small amount of residual ethoxide (see Table 3). The resonances at 27 and 18.9 ppm (^{13}C NMR of PPS and EPS, respectively) and −66 ppm (^{29}Si NMR) show that both phosphorus–carbon and silicon–carbon bonds within the $-Si(CH_2)_nPO(OH)_2$ units are present.

The broad resonance around 34 ppm in the ^{31}P spectra of P1 and P2 attributed to the fragment $-(CH_2)_nPO(OCH_2CH_3)_2$ is shifted slightly downfield to 32 ppm for the corresponding acids, $-(CH_2)_nPO(OH)_2$, in PPS and EPS. In addition to the resonances at 34 and 32 ppm assigned to phosphonate and phosphonic acid, respectively, ^{31}P resonances around *ca.* 23 ppm appeared in the spectra of all the materials P1, P2, PPS and EPS (and P3, P4, PPSilses, and EPSilses, discussed later) varying from trace quantities (see P3) up to one fifth (see P1) the intensity of the resonances at 34 ppm. ^{31}P chemical shift values for $XCH_2PO(OR)_2$ (R = Et/H) compounds are markedly dependant on nature of X, *e.g.* R = Et; X = CH_3, CO_2H ^{31}P 37.0, 24 ppm, respectively (both measured in water).[5] Following the sol–gel reaction carefully by NMR shows that the ^{31}P resonances around 24 ppm appear after gelation only, which suggests that they may be a consequence of surface interactions between the phosphonate groups and the framework. These resonances are not present in either of the starting compounds **1** or **2**, nor do they appear in the free-flowing sol mixtures leading to P1 and P2 but appear only after further processing of samples (ageing, solvent treatment and drying). The reaction conditions leading to P1 and P2 (or P3 and P4, see later) are too mild to effect any chemical cleavage of P–C or Si–C bonds and, in any case, the chemical shift of *ca.* 23 ppm is inconsistent with a by-product of this type. Furthermore, the measured T/Q ratios in P1, P2, PPS or EPS do not indicate any Si–C cleavage. It is reasonable to expect that $PO(OR)_2$ (R = Et/H) groups in T-functionalised phosphonate and phosphonic acid moieties, $-(RO)_{3-n}O_{n/2}Si(CH_2)_nPO(OR)_2$ (R = Et/H), constrained within irregular frameworks having variable distribution and numbers of surface hydroxy groups, may be present as the free moiety or be engaged in H-bonding with the surface hydroxy groups and thus more than one phosphorus environment might be expected. The random variations in intensity of the resonances around 23 ppm found in the different materials supports this.

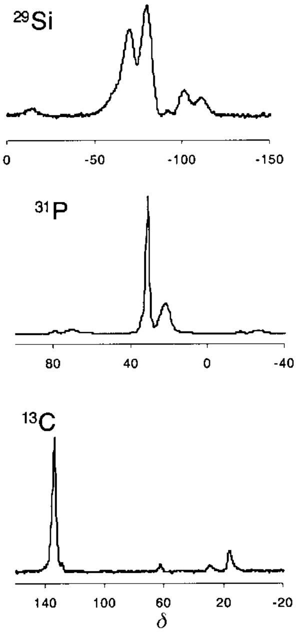

Fig. 4 Solid state ^{29}Si, ^{31}P and ^{13}C NMR spectra for PPSilses.

Table 2 NMR data for P3, P4, PPSilses and EPSilses

NMR		P3	P4	PPSilses	EPSilses
^{29}Si	T^1	−61.9			
	T^2	−67.0	−70.0	−70.4	−70.6
	T^3	−78.1	−77.3	−79.7	−79.7
	Q^2			−92.3	−91.7
	Q^3			−101.1	−101.4
	Q^4			−108.7	−110.3
^{31}P		22.3 (trace)	23.7	22.2	22.8
		34.0	33.2	31.2	32.1
^{13}C		16.4	5.0	16.4	5.8
		28.2	16.0	29.7	21.2
		63.1	62.6	62.4	62.8
		134.0	133.7	133.7	133.7

Assignment of stoichiometric formulae for P1, P2, PPS and EPS based on deconvoluted NMR spectroscopic data and elemental analyses are given in Table 3.

Materials from BTESB and $[(EtO)_3Si(CH_2)_3PO(OEt)_2]$ 1 or $[(EtO)_3Si(CH_2)_2PO(OEt)_2]$ 2

A similar series of co-polymerisation experiments with BTESB [1,4-bis(triethoxysilyl)benzene, *p*-$\{(EtO)_3Si\}_2C_6H_4$], and **1** or **2** (4 : 1 molar ratio in THF with dilute acid catalysis) gave transparent gels which dried to give transparent glasses P3 and P4.

The solid state CP MAS ^{29}Si,‡ ^{31}P, and ^{13}C NMR spectra, for P3 are shown in Fig. 3 and confirm the presence of the spacer benzene group and the phosphonate ester moiety. Further treatment of these xerogels with concentrated HCl gave the corresponding propylphosphonic acid-modified silsesquioxane gel PPSilses and ethylphosphonic acid-modified silsesquioxane gel EPSilses (NMR spectra for P3 and PPSilses are shown in Figs. 3 and 4). NMR data for P3, P4, PPSilses and EPSilses are given in Table 2.

Solid state NMR studies

NMR spectroscopic data for P3, P4, PPSilses and EPSilses are summarised in Table 2 and assignments discussed below.

The co-polymerised materials P3 and P4 had the expected resonances for the organic components of the materials in their solid state ^{13}C NMR spectra. As found for P1, the peaks due to the ester groups in P3 occur around δ 16(broad) and 63 (^{13}C NMR) and the broad resonance around 16 ppm masks the

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‡Recycle delay 5 ms. ^{29}Si spectra were also measured using SPE MAS (see Fig. 5 and related discussion).

Table 3 Average stoichiometric formulae from deconvoluted ^{29}Si CP MAS and SPE MAS NMR spectra, and elemental analyses

Material	Formula from deconvoluted ^{29}Si NMR and C : P ratios	α^a	β^b	C : P calc.	C : P found
P1	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_3PO(OEt)_2]_y$[c] $[(RO)_{0.64}O_{1.68}Si]_{10}[(RO)_{1.26}O_{0.87}Si(CH_2)_3PO(OEt)_2]$[d] $[(HO)_{0.56}(EtO)_{0.08}O_{1.68}Si]_{10}[(HO)_{1.26}O_{0.87}Si(CH_2)_3PO(OEt)_2]$[e] $C_{8.5}H_{27.5}O_{28.4}Si_{11}P$	58	84	2.7 (R = H) 3.3	3.3
PPS	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_3PO(OH)_2]_y$[c] $[(RO)_{0.4}O_{1.8}Si]_{10}[(RO)_{1.02}O_{0.99}Si(CH_2)_3PO(OH)_2]$[d] $[(HO)_{0.34}(EtO)_{0.06}O_{1.8}Si]_{10}[(HO)_{1.02}O_{0.99}Si(CH_2)_3PO(OH)_2]$[d] $C_{4.2}H_{15.6}O_{27}Si_{11}P$	66	90	1.2 (R = H) 1.6	1.6
P2	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OEt)_2]_y$[c] $[(RO)_{0.76}O_{1.62}Si]_{10}[(RO)_{1.29}O_{0.86}Si(CH_2)_2PO(Oet)_2]$[d] $[(HO)_{0.7}(EtO)_{0.06}O_{1.62}Si]_{10}[(HO)_{1.29}O_{0.86}Si(CH_2)_2PO(OEt)_2]$[e] $C_{7.2}H_{26.1}O_{29}Si_{11}P$	57	81	2.3 (R = H) 2.8	2.8
EPS	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OH)_2]_y$[c] $[(RO)_{0.36}O_{1.82}Si]_{10}[(RO)_{1.02}O_{0.99}Si(CH_2)_2PO(OH)_2]$[d] $[(HO)_{0.28}(EtO)_{0.08}O_{1.82}Si]_{10}[(HO)_{1.02}O_{0.99}Si(CH_2)_2PO(OH)_2]$[e] $C_{3.6}H_{13.8}O_{26.8}Si_{11}P$	66	91	0.78 (R = H) 1.35	1.35
P3	$[(RO)_{6-2n}O_nSi_2C_6H_4]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_3PO(OEt)_2]_y$[c] $[(HO)_{1.98}O_{2.01}Si_2C_6H_4]_{3.5}[(HO)_{0.99}O_{1.01}Si(CH_2)_3PO(OEt)_2]$[f] $C_{28}H_{38}O_{19}Si_8P$	67		10.9	10.9
PPSilses	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{6-2n}O_nSi_2C_6H_4]_y[(RO)_{3-n}O_{n/2}Si(CH_2)_3PO(OH)_2]_z$ [c] $[(HO)_{0.8}O_{1.6}Si]_{1.76}[(HO)_{1.14}O_{2.43}Si_2C_6H_4]_{2.5}[(HO)_{0.57}O_{1.22}Si(CH_2)_3PO(OH)_2]$[g] $C_{18}H_{22}O_{13.4}Si_{7.7}P$	81	80	6.9	6.9
P4	$[(RO)_{6-2n}O_nSi_2C_6H_4]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OEt)_2]_y$[c] $[(HO)_{1.74}O_{2.13}Si_2C_6H_4]_{3.4}[(HO)_{0.87}O_{1.07}Si(CH_2)_2PO(OEt)_2]$[f] $C_{26.4}H_{34.4}O_{18.1}Si_{7.8}P$	71		10.2	10.2

carbon environments α and β to silicon ($-SiCH_2CH_2CH_2P-$) while the carbon α to phosphorus [$-Si(CH_2)_2CH_2P-$] appears at 27 ppm, as in **1**. The resonances at 134 ppm result from the aromatic carbons of BTESB.

In comparison with the ^{13}C NMR spectrum of P2, P4 has a peak at δ 5 which we assign to the carbon α to silicon [$-SiCH_2CH_2P-$]; the phosphonate ester groups and residual silyl ester groups appear at 16 and 62 ppm, respectively, with the former masking the carbon α to phosphorus in $-SiCH_2CH_2PO(OCH_2CH_3)_2$. The aromatic carbons in P4 resonate at 134 ppm. Two ^{31}P resonances at δ *ca.* 22 and 34 are seen for P3 and P4 (as for P1and P2, see discussion above) with the relative intensity of the former again varying from a trace to about one fifth of the lower field resonance. The ^{29}Si shows only T^n environments for materials P3 and P4, indicating that no Si–C cleavage has occurred (further evidence that the phosphorus-containing species resonating at 22 ppm in the ^{31}P NMR spectra is not derived from Si–C cleavage). Both P3 and P4 are essentially non-porous.

Hydrolysis of P3 and P4 with concentrated HCl, gave PPSilses and EPSilses. The ^{31}P resonance at 34 ppm due to the phosphonate ester is absent in the acid-treated materials. The distribution of T^n resonances was considerably altered following concentrated hydrochloric acid treatment and, in addition, the appearance of Q^n resonances in the ^{29}Si NMR spectra of PPSilses and EPSilses indicates a small amount of Si–C(Aryl) cleavage. The Q^n environments in the formulae for PPSilses and EPSilses (Table 3) are attributed to Si–C(sp^2) cleavage only, based on the expected relative reactivity of Si–C(sp^2) compared to Si–C(sp^3) and the absence of any Si–C(sp^3) cleavage products in EPS and PPS. The resonances at 29 and 21 ppm in the ^{13}C NMR spectra of PPSilses and EPSilses, respectively, indicate that the P–C bonds in $[(RO)_{3-n}O_{n/2}Si(CH_2)_nPO(OH)_2]$ are intact.

A striking consequence of the conversion of phosphonate esters P3 and P4 to phosphonic acids PPS and EPS was their transformation from non-porous phosphonate esters ($S < 10\ m^2\ g^{-1}$) to porous ($S > 450\ m^2\ g^{-1}$) phosphonic acids. This may in part be a consequence of the removal of the phosphonate ester groups.

The degrees of condensation, α for T^n and β for Q^n sites in the new materials (evaluated from deconvoluted ^{29}Si NMR data), were used in conjunction with experimentally determined carbon : phosphorus and, if appropriate, $T^n : Q^n$ ratios, to derive the stoichiometric formulae for P1–P4, PPS, EPS, PPSilses and Epsilses as shown in Table 3. In samples P1, P2, EPS and PPS, containing both T^n and Q^n environments, the relative areas of the T and Q sites and the site occupancies within the T^n and Q^n groups were dramatically different for spectra recorded using CP MAS and SPE (single pulse excitation) MAS NMR§ (see Fig. 5). The differences are slight for the PPSilses and EPSilses materials, where the measured ratio T/Q = 3.4 is relatively high. SPE MAS is quantitatively more reliable that CP MAS and, therefore, the degrees of condensation quoted are based on site occupancies derived from SPE MAS spectra in these cases. For samples containing only T^n sites the results were similar for the CP

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§Recycle delay for CP MAS 2 ms, for SPE MAS 60 s

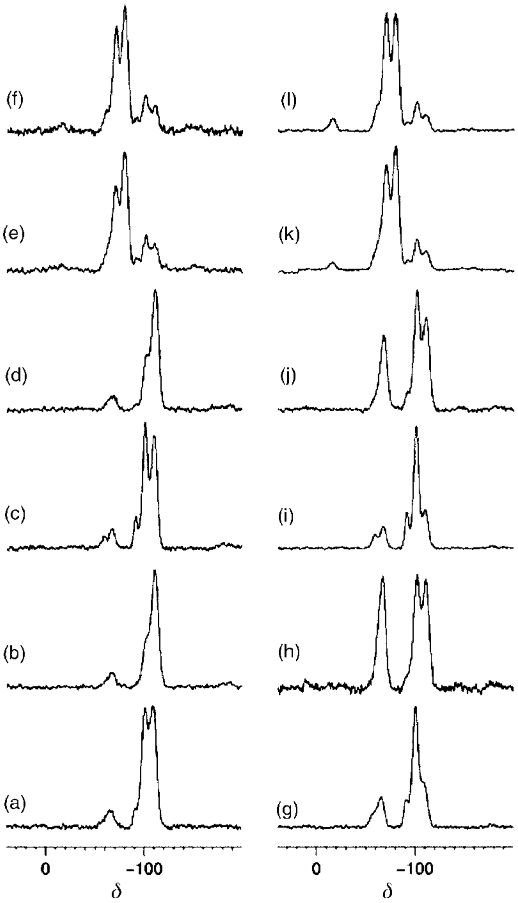

Fig. 5 Comparison of ^{29}Si NMR spectra obtained using SPE MAS (left) and CP MAS (right) (a),(g) P1; (b),(h) PPS; (c),(i) P2; (d),(j) EPS; (e),(k) PPSilses; (f),(l) EPSilses.

MAS and SPE MAS spectra. This was previously observed to be the case for various polysilsesquioxanes.[6]

Nitrogen porosimetry studies

Porosity measurements on samples of EPS, PPS, PPSilses and EPSilses were performed using nitrogen sorption and the results are summarized in Table 4.

The porosity of these samples is relatively high. There are marked changes in texture from P1and P2, which are essentially microporous, to PPS and EPS which are essentially mesoporous. The increase in average pore size may in part be attributed to the removal of the phosphonate ester groups. We noted earlier that both P3 and P4 were essentially non-porous, but the phosphonic acid materials PPSilses and EPSilses have relatively high levels of porosity. The two sets of samples PPS, EPS and PPSilses, EPSilses, display interesting and different types of pore structure. The two samples PPS and EPS are uniformly mesoporous, while the two samples PPSilses and EPSilses have both meso and microporous character.

Table 4 Porosity measurement results for PPS, EPS, PPSilses and EPSilses

Material	BET surface area/m^2 g^{-1}	Micropore surface area/m^2 g^{-1}	Micropore volume/ cm^3 g^{-1}	Total pore volume/ cm^3 g^{-1}
P1	424	416	0.25	0.26
PPS	350	N/A	N/A	0.38
P2	240	225	0.12	0.15
EPS	600	30	0.01	1.37
PPSilses	563	533	0.34	0.40
EPSilses	477	439	0.24	0.31

The adsorption–desorption isotherms of samples P1, PPS and PPSilses are shown in Figs. 6, 7 and 8, respectively. A typical type E hysteresis[7] was found for PPS, suggesting ink-bottle shaped pore structure. In keeping with this, there is a marked step in the desorption curve between 0.42 and 0.48 P/P_0. Type E hysteresis was also found for PPSilses and EPSilses, although with much smaller hysteresis loops. This also suggests an ink-bottle pore structure, although with a bigger pore opening than for PPS. It was not possible to perform a de Boer *t*-calculation[8] on the PPS data; there is no defined linear region on the *V*/*t* plot in keeping with the absence of micropores. The BJH[9] pore size distribution in PPS shown in Fig. 6a, is very narrow and in the mesopore region, between 31–41 Å. Such a uniform distribution suggests some kind of templating effect may be operating during synthesis. In contrast, the BJH pore size distribution in PPSilses in Fig. 7a and EPSilses is bi-modal

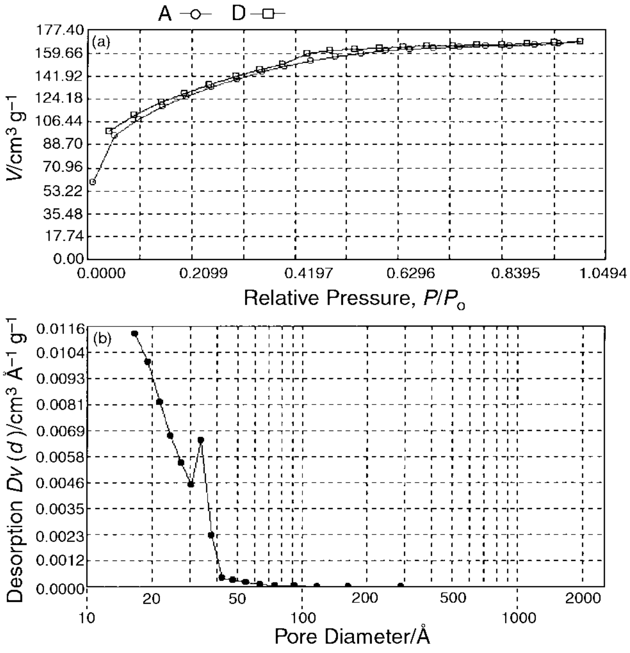

Fig. 6 (a) Nitrogen adsorption–desorption Isotherms for P1. (b) BJH pore size distribution for P1.

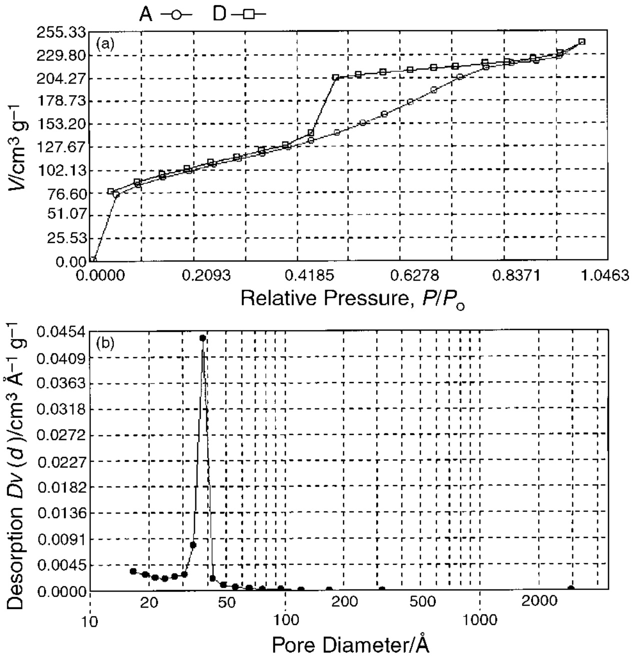

Fig. 7 (a) Nitrogen adsorption–desorption Isotherms for PPS. (b) BJH pore size distribution for PPS.

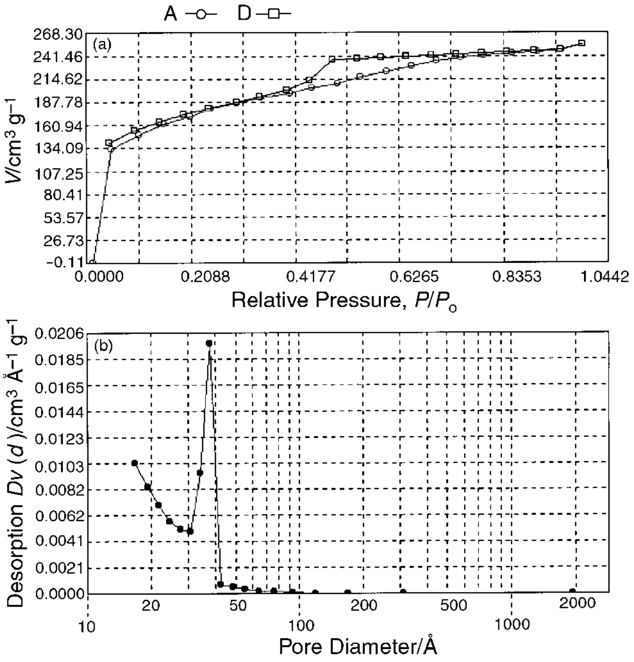

Fig. 8 (a) Nitrogen adsorption–desorption Isotherms for PPSilses. (b) BJH pore size distribution for PPSilses.

over the micro and mesopore regions (distribution 30 to 40 Å in the latter case).

Conclusion

We have described work leading to the first examples of silica and polysilsesquioxane materials having covalently attached phosphonate and phosphonic acid groups. Conversion of the covalently attached phosphonate ester to the corresponding acids was achieved with minimal apparent loss of T-functionalised ligand through Si–C or P–C cleavage. Surface area measurements indicate that, with the exception of the phosphonate-modified silsesquioxanes, the new materials are porous. The narrow mesopore range exhibited by the phosphonic acid-modified silicas is interesting and contrasts with the bi-modal distribution of micro and mesopores found in the polysilsesquioxane-modified materials.

We are currently investigating the acid-catalytic activity and the coordination chemistry of these and other related phosphonic acid-modified silicas and polysilsesquioxanes, the latter with a view to applications in catalysis and separation processes.

Experimental

Manipulations of air-sensitive compounds were carried out under an atmosphere of dinitrogen using standard Schlenk-line techniques. Solvents were refluxed over an appropriate drying agent and degassed prior to use. Solution state NMR spectra were recorded from $CDCl_3$ solutions using Bruker 250 MHz, 400 MHz, and AMX 600 MHz spectrometers. All solid state NMR spectra (^{29}Si CP MAS and SPE MAS, frequency 59.6 MHz; ^{13}C CP MAS, frequency 75.5 MHz; ^{31}P CP MAS, frequency 121.5 MHz) were recorded on a Bruker MSL 300 MHz spectrometer, spinning speed 4.7 kHz. Typical conditions for CP MAS were (^{29}Si 5 ms contact time, 1 s delay, 90° pulse for 4.5 μs, ^{13}C 1 ms contact time, 2 s delay, 90° pulse for 4.8 μs; ^{31}P 10 ms contact time, 1.5 s delay 90° pulse for 3.5 μs). ^{29}Si SPE MAS spectra were acquired using 1 min recycle delay, with 40° pulse.

Microanalyses were obtained from the analytical services at Queen Mary and Westfield College, and University College London. Surface area measurements were recorded using a Micromeritics Flowsorb II 2300 surface area analyser and nitrogen sorption porosimetry measurements were performed using a Quanta Chrome Autosorb 1MP system. The xerogels were ground into fine powders then degassed for several hours. Surface areas were determined by the BET method.[10] Pore size distributions in the mesopore region were determined by the BJH method.[9] The de Boer *t*-method[8] was used to evaluate the micropore volume.

The starting reagent $(EtO)_3SiC_6H_4Si(OEt)_3$, BTESB, was synthesised according to literature method.[11] Spectroscopic and analytical data for **1** and **2** (not previously reported) have been measured for this work and are given below with appropriate assignments.

Syntheses

$[(EtO)_3Si(CH_2)_3PO(OEt)_2]$ 1[4]. ^{1}H NMR (400 MHz) $[(C^1H_3C^2H_2O)_3SiC^3H_2C^4H_2C^5H_2PO(OC^6H_2C^7H_3)_2]$ (superscripted numbers distinguish hydrogen environments): δ 0.7 (t, 2H, ^{3}H, $^3J_{HH}$ 8 Hz), 1.2 (t, 9H, ^{1}H, $^3J_{HH}$ 8 Hz), 1.3 (t, 6H, ^{7}H, $^3J_{HH}$ 8 Hz), 1.7 (overlapping multiplets, 4H, ^{4,5}H), 3.8 (q, 6H, ^{2}H, $^3J_{HH}$ 8 Hz), 4.0 (m, 4H, ^{6}H, $^3J_{PH}$ 10 Hz); ^{13}C NMR (100.58 MHz) $[(C_aH_3C_bH_2O)_3SiC_cH_2C_dH_2C_eH_2PO(OC_fH_2C_gH_3)_2]$ (subscripted letters distinguish carbon environments): δ 12.1, 12.2 (d, C_d, $^2J_{PC_d}$ 16 Hz) 16.8 (d, C_c , $^3J_{PC_c}$ 4.6 Hz), 16.9 (d, C_g, $^3J_{PC_g}$ 7.5 Hz), 18.2 (s, C_a), 28.8, 29.8 (d, C_e, J_{PC_e} 138.2 Hz), 58.9 (s, C_b), 61.7, 61.8 (d, C_f, $^2J_{PC_f}$ 6.3 Hz); ^{29}Si NMR (79.5 MHz): δ −44.8; ^{31}P{^{1}H} NMR (161.9 MHz) 32.6 (s). Found: C, 44.1; H, 8.9; $C_{13}H_{31}PO_6Si$ requires: C, 45.6; H, 9.1%.

$[(EtO)_3Si(CH_2)_2PO(OEt)_2]$ 2[4]. ^{1}H NMR (400 MHz) $[(C^1H_3C^2H_2O)_3SiC^3H_2C^4H_2PO(OC^5H_2C^6H_3)_2]$ (superscripted numbers distinguish hydrogen environments): δ 0.7 (m, 2H, ^{3}H, $^3J_{PH}$ 10 Hz), 1.1 (t, 9H, ^{1}H, $^3J_{HH}$ 8 Hz), 1.1 (t, 6H, ^{6}H, $^3J_{HH}$ 8 Hz) 1.6 (m, 2H, ^{4}H, $^2J_{PH}$ 18 Hz), 3.6 (q, 6H, ^{2}H, $^3J_{HH}$ 8 Hz), 3.9 (m, 4H, ^{5}H, $^3J_{PH}$ 10 Hz);^{13}C NMR (100.58 MHz) $[(C_aH_3C_bH_2O)_3SiC_cH_2C_dH_2PO(OC_eH_2C_fH_3)_2]$ (subscripted letters distinguish carbon environments): δ 2.8 (d, C_c, $^2J_{PC_c}$ 8.3 Hz), 16.8 (d, C_f, $^3J_{PC_f}$ 5.2 Hz), 18.6 (s, C_a), 18.4, 19.1 (d, C_d, J_{PC_d} 141.7 Hz), 61.8 (s, C_b), 61.9 (d, C_e, $^2J_{PC_e}$ 2.5 Hz); ^{29}Si NMR (79.5 MHz): δ 47.7 (d, $^3J\{^{29}Si,^{31}P\}$ 45 Hz); ^{31}P{^{1}H} NMR (161.9 MHz): δ 34.5 (s). Found: C, 43.5; H, 8.8; $C_{12}H_{29}PO_6Si$ requires: C, 43.9; H, 8.9%

Co-polymerisation of TEOS–1 (4:1)

The reagents TEOS (6.93 g, 33.2 mmol), **1** (2.84 g, 8.3 mmol), ethanol (1.53 g, 33.2 mmol), HCl (3.30 ml, 0.1 M, 0.332 mmol) and water (8.70 ml) were combined under N_2. The mixture was stirred for 30 min to give a clear solution. This sol was left under dinitrogen for 24 h and then exposed to air. The gel obtained was air-dried for 1 week and then dried at 60 °C in an oven for 24 h. A two-phase material, consisting of a transparent glassy phase and an opaque phase, was produced. This was heated to 120 °C under vacuum for several hours to remove any volatiles. $S = 9$ m^2 g^{-1}. ^{31}P CP MAS NMR: δ 33.1 (s), 22.0 (broad s, trace amount); ^{29}Si CP MAS NMR: δ −65.2, −101.3, −110.0; ^{13}C CP MAS NMR: δ 16.7, 27.4, 63.5.

Co-polymerisation of TEOS–2 (4:1)

The reagents TEOS (6.93 g, 33.2 mmol, 7.42 ml), **2** (2.73 g, 8.3 mmol, 2.42 ml), ethanol (1.53 g, 33.2 mmol, 1.95 ml), HCl (3.30 ml, 0.1 M, 0.332 mmol) and water (8.70 ml) were combined under N_2 and treated as described above to give a 2-phase material. $S = 8$ m^2 g^{-1}. ^{13}C CP MAS NMR: δ 4.8, 16.6, 63.6; ^{31}P CP MAS NMR: δ 34.3 (s), 22.0 (broad singlet, trace amount); ^{29}Si CP MAS NMR: δ −66.7, −91.6, −100.8, −109.4.

P1: co-polymerisation of TEOS–1 (10 : 1)

The reagents TEOS (6.93 g, 33.2 mmol, 7.42 ml), **1** (1.13 g, 3.3 mmol), ethanol (1.53 g, 33.2 mmol), HCl (3.30 ml, 0.1 M, 0.33 mmol) and H_2O (8.70 ml) were combined under N_2. The immiscible mixture was stirred for 30 min to give a clear solution. This sol was left under dinitrogen for 24 h and then exposed to air. Once gelled, the sample was air dried for 1 week and then dried at 60 °C in an oven for 24 h. A clear monophasic material was produced. This was crushed into a fine powder and washed with water, ethanol and ether consecutively, and then dried under vacuum at 120 °C for 24 h. $S = 453\ m^2\ g^{-1}$

P2: co-polymerisation of TEOS–2 (10 : 1)

The reagents TEOS (6.93 g, 33.2 mmol, 7.42 ml), **2** (1.09 g, 3.3 mmol), ethanol (1.53 g, 33.2 mmol), HCl (3.30 ml, 0.1 M, 0.33 mmol) and H_2O (8.70 ml) were combined under N_2 and treated as described for P1. $S = 143\ m^2\ g^{-1}$.

PPS: HCl hydrolysis of P1

Powdered P1 (0.50 g) and concentrated HCl (50 ml) were refluxed for 24 h. The mixture was filtered through a fritted funnel and washed with excess H_2O to remove all traces of HCl, and then with ethanol and ether. The residue was dried under vacuum at 120 °C for 24 h.

EPS: HCl hydrolysis of P2

Powdered P2 was treated as described above for P1.

P3: co-polymerisation of 1–BTESB (1 : 4)

The reagents 1,4-bis(triethoxysilyl)benzene (3.45 g, 8.6 mmol, 2.90 ml), **1** (0.74 g, 2.15 mmol), THF (37 ml) and HCl (0.8 ml, 1 M) were combined under N_2. The mixture was stirred for 30 min to give a clear solution. The sol was left under dinitrogen for 24 h. The gel obtained was air-dried for 1 week and then dried at 60 °C in an oven for 24 h. A transparent glass was produced. This was heated to 120 °C under vacuum for several hours to remove any volatiles. $S = 7\ m^2\ g^{-1}$

P4: co-polymerisation of 2–BTESB (1 : 4)

The reagents 1,4-bis(triethoxysilyl)benzene (3.45 g, 8.6 mmol, 2.90 ml), **2** (0.71 g, 2.15 mmol,), THF (37 ml) and HCl (0.8 ml, 1 M) were combined under N_2 and treated as described for P3. $S = 8\ m^2\ g^{-1}$

PPSilses: HCl hydrolysis of P3

Powdered P3 (0.50 g) and concentrated HCl (50 ml) were refluxed for 24 h. The mixture was filtered through a fritted funnel and washed with excess H_2O to remove all traces of HCl and then with ethanol and ether. The residue was dried under vacuum at 120 °C for 24 h.

EPSilses: HCl hydrolysis of P4

Method as for PPSilses above.

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