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Synthesis, characterisation and catalytic activity of porous vanadyl phosphonate-modified silicas

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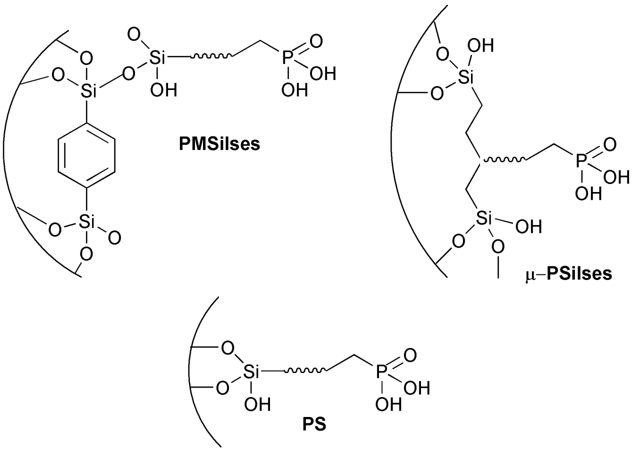
Synthetic routes to porous ethylphosphonic acid-modified silicas with high T/Q ratios are described. The resulting materials were characterised using ^{29}Si, ^{31}P and ^{13}C solid state NMR, nitrogen sorption porosimetry and elemental analysis. In addition, conditions for post-modification using [VO(SO$_4$)·5H$_2$O] are described; the vanadyl derivatives were characterised by porosimetry, elemental analysis, EPR and UV-Vis spectroscopy. One of these vanadyl derivatives is a useful catalyst for the oxidation of *cis*-cyclooctene using aqueous hydrogen peroxide as the oxidant.

Introduction

Mesoporous solid acid and base catalysts are increasingly being discussed as environmentally benign alternatives to liquid phase Brønsted and Lewis acid catalysts, and the field has been reviewed.[1] A range of materials, including zeolites, phosphates, clays and various sulfonated polymers, belong to the solid acid category. Industrial catalytic processes using these catalysts include dehydration and condensation, isomerisation, alkylation, cracking, hydration, and esterification reactions. There has been considerable recent interest in silica materials with covalently bonded sulfonic acid functions.[2]

We recently reported on the first members of new families of phosphonic acid-modified silicas (PS), polysilsesquioxanes (PSilses) and phosphonic acid-bridged polysilsesquioxanes (μ-PSilses) (Scheme 1).[3] Phosphonic acid groups are particularly attractive in that they offer a strong binding site for catalytic metal ions and this aspect of the chemistry of some new phosphonic acid-modified silicas is described herein. To our knowledge, this work represents the first descripition of the synthesis and chemistry of metal phosphonate-modified silicas.



Scheme 1

Results and discussion

Synthesis of phosphonic acid-modified silicas with high T/Q ratios

Under the conditions we reported in our earlier paper,[3] transparent xerogels of propyl and ethylphosphonate ester-modified silica, PPES and EPES, could only be obtained for relatively low phosphonate ester loading {*e.g.* TEOS/PE ≈ 10; abbreviated to PPES10 and EPES10, where PPE is [(EtO)$_3$Si(CH$_2$)$_3$PO(OEt)$_2$] and EPE is [(EtO)$_3$Si(CH$_2$)$_2$PO(OEt)$_2$]}. At higher loading, for example, PPES4 and EPES4, there was apparent phase separation with formation of opaque and transparent regions within the monolithic gels. We now report that transparent PES materials can be obtained without any apparent phase separation, even at TEOS/PE ratios <1, provided all steps of the sol–gel process, gelation, aging and drying are carried out at 60 °C, instead of room temperature as previously described.[3] EPES materials processed in ethanol and methanol were prepared and converted to the corresponding phosphonic acid-modified silicas, EPSe and EPSm, by treatment with concentrated HCl. Details of the synthesis conditions for the phosphonate ester-modified silicas are given in Table 1.

Table 1 Conditions for the synthesis of phosphonate ester (PES) materials

	PE/mmol	TEOS/mmol	EtOH/cm^3	MeOH/cm^3	1 M HCl/cm^3
EPESe1[a]	17.9	19.3	37.2	—	9.3
EPESe2	15.0	30.3	45.3	—	11.3
EPESe3	11.9	39.3	51.2	—	12.8
EPESm1	16.2	17.5	—	33.7	8.4
EPESm2	14.2	28.6	—	42.8	10.7
EPESm3	12.8	41.0	—	53.8	13.4

[a]EPESe1 denotes *e*thyl*p*hosphonate *e*ster-modified *s*ilica processed in *e*thanol, TEOS : PE ≈ *1*. The PES materials were converted to the corresponding phosphonic acid-modified silicas (PS) by treatment with conc. HCl.

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Table 2 Pore structure parameters for the EPS series of materials

Entry	BET surface area/$m^2\ g^{-1}$	Micropore surface area (t-method)/$m^2\ g^{-1}$	Cumulative desorption BJH surface area/$m^2\ g^{-1}$	Micropore (total pore) volume/$cm^3\ g^{-1}$	Mean pore diameter/Å
EPSe1	42	—	—	—	—
EPSe2	486	168	370	0.08 (0.25)	20
EPSe3	607	74	735	0.04 (0.36)	24
EPSm1	4	—	—	—	—
EPSm2	441	1.2	492	0.0 (0.25)	22
EPSm3	609	0.0	684	0.0 (0.4)	26

Nitrogen porosimetry studies on EPSe and EPSm materials

Porosity measurements on the EPSe1–EPSe3 and EPSm1–EPSm3 samples were performed using nitrogen sorption porosimetry. The results are summarised in Table 2. The sorption isotherms are shown in Fig. 1 and 2. Variation of the T/Q ratio has a marked effect. The EPSe1 and EPSm1 materials prepared at 60 °C are relatively non-porous. The corresponding EPS2 and EPS3 materials have relatively high surface areas with the ethanol processed materials having the slightly lower values of the two. There is a striking change (reproduced several times) in the shape of the isotherms from EPSe3 to EPSe10 (see Fig. 2). Overall, the nitrogen sorption isotherms for the EPS materials with the same T/Q ratios prepared in ethanol and methanol (Fig. 1) are very similar, showing that slight differences in solvent polarity and volatility have a negligible effect. As we previously reported,[3] porisimetry indicated that room temperature-processed propylphosphonic acid-modified silica (PPSe10) displayed very different textural properties to the related EPSe10, but the material was nonetheless mesoporous with a surface area of ~300 $m^2\ g^{-1}$. In contrast to the EPSe2/EPSe3 and EPSm2/EPSm3 materials prepared at 60 °C, we found the corresponding series of PPSe and PPSm materials prepared under identical conditions to be non-porous. This may be a reflection of the greater steric demand of the C_3 fragment at high loading. Following our initial paper on these materials,[3] Durand *et al.* have reported[4] EPS materials using Me_3SiBr instead of HCl to convert the phosphonate ester to the phosphonic acid. It is noteworthy that the materials prepared using Me_3SiBr are non-porous, in contrast to the results we report here for high loaded EPSe2/EPSe3 and EPSm2/EPSm3.

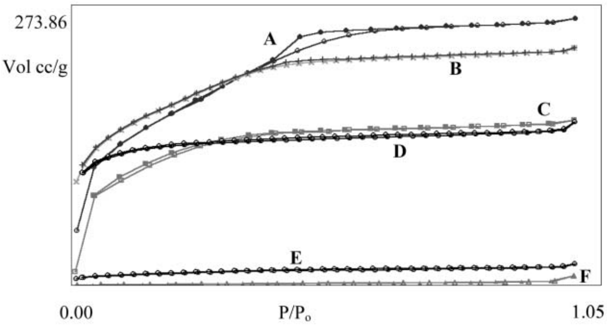

Fig. 1 Nitrogen sorption isotherms for the EPSm3, EPSm2 and EPSm1 (A, C and E), and EPSe3, EPSe2 and EPSe1 (B, D and F) series of materials.

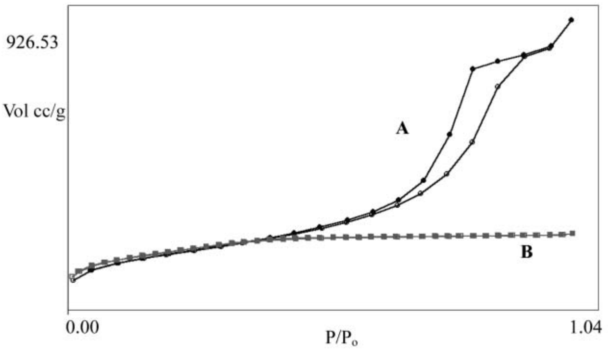

Fig. 2 Nitrogen sorption isotherms for EPSe10 (A) and EPSe3 (B).

Spectroscopic characterisation of EPS materials. The solid state NMR spectroscopic details of the EPS series of materials are given in Table 3. The data confirm the presence of the expected T and Q environments for all the materials. As previously seen for the EPSe10 material,[3] in addition to the major signal due to $-PO(OH)_2$ at ~32 ppm, there is a relatively small signal at ~23 ppm in the ^{31}P MAS NMR spectra, indicating that some $-PO(OH)_2$ groups are likely interacting with surface silanol, *i.e.* Si–OH···O=P. Condensation levels within the Q environments are generally high, while within T environments, there is a slight decrease in overall condensation as loading increases, as shown in Table 4. All materials show resonances due to small amounts of unhydrolysed ethoxy groups. There is generally very good agreement between $-PO(OH)_2$ loading values based on average formulae derived from the NMR data (which exclude any retained or adsorbed water) and loading values based simply on the measured percentages of phosphorus in the dried materials. The materials were carefully dried under vacuum and subsequently stored and weighed under nitrogen prior to elemental analysis, so they were essentially anhydrous when analysed. They are, however, very hygroscopic. On standing in air for one month, both EPSe3 and EPSe1 were found to absorb ~0.28 g of water per g of material, which corresponds to 4–5 equivalents of water per $-PO(OH)_2$ unit.

Table 3 Solid state NMR spectroscopic data for EPS materials

NMR	Assignment	EPSe1	EpSe2	EPSe3	EPSm1	EPSm2	EPSm3
^{29}Si SPE MAS	T^1	−59.6	−64.2	—	−60.0	−63.9	—
	T^2	−67.4	−67.9	−67.7	−68.0	−66.8	−67.9
	Q^3	−101.2	−103.4	−101.7	−102.2	−102.2	−101.9
	Q^4	−110.7	−110.2	−110.1	−110.8	−110.2	−110.5
^{31}P CP MAS		32.2	32.1	32.1	31.8	31.8	31.3
		22.7	22.5	22.8	20.9	20.9	21.1
^{13}C CP MAS	CH_2Si	5.5	5.3	5.3	5.7	5.3	5.0
	CH_2P	20.9	20.8	19.8	20.3	19.8	19.8
	$CH_3\mathit{CH}_2O$	58.8	58.8	58.3	58.5	58.4	58.4

Table 4 Average stoichiometric formulae for EPS materials from deconvoluted ^{29}Si SPE MAS NMR spectra and elemental analyses

	Formulae from ^{29}Si NMR and C : P ratios	α^a	β^b	C/P calc.	C/P found	–$PO(OH)_2$ loading calc.^{c} (found^d)/mmol g^{-1}
EPSe1	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OH)_2]^e$					
	$[(RO)_{0.30}O_{1.85}Si]_{1.1}[(RO)_{1.20}O_{0.90}Si(CH_2)_2PO(OH)_2]^f$	60	93	0.78 (R = H)		
	$[(HO)_{0.30}O_{1.85}Si]_{1.1}[(HO)_{0.6}(EtO)_{0.6}O_{0.90}Si(CH_2)_2PO(OH)_2]^g$			1.24	1.24	
	$C_{3.2}H_{9.99}O_{7.47}Si_{2.1}P^h$					3.9 (4.00)
EPSe2	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OH)_2]^e$					
	$[(RO)_{0.32}O_{1.84}Si]_{2.0}[(RO)_{1.23}O_{0.89}Si(CH_2)_2PO(OH)_2]^f$	59	92	0.78 (R = H)		
	$[(EtO)_{0.03}(HO)_{0.29}O_{1.84}Si]_{2.0}[(HO)_{1.23}O_{0.89}Si(CH_2)_2PO(OH)_2]^g$			0.82	0.82	
	$C_{2.12}H_{8.11}O_{9.12}Si_3P^h$					3.3 (3.4)
EPSe3	$[(RO)_{4-n}O_{n/2}Si]_x[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OH)_2]^e$					
	$[(RO)_{0.24}O_{1.88}Si]_{3.3}[(RO)_{0.99}O_{1.01}Si(CH_2)_2PO(OH)_2]^f$	67	94	0.78 (R = H)		
	$[(EtO)_{0.16}(HO)_{0.08}O_{1.88}Si]_{3.3}[(HO)_{0.99}O_{1.01}Si(CH_2)_2PO(OH)_2]^g$			1.19	1.19	
	$C_{3.06}H_{9.89}O_{12.00}Si_{4.3}P^h$					2.6 (2.6)
EPSm1	$[(RO)_{4-n}O_{n/2}Si]_{1.0}[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OH)_2]^e$					
	$[(RO)_{0.32}O_{1.84}Si]_{1.0}[(RO)_{1.29}O_{0.86}Si(CH_2)_2PO(OH)_2]^f$	57	92	0.78 (R = H)		
	$[(EtO)_{0.17}(HO)_{0.15}O_{1.84}Si]_{1.0}[(HO)_{1.29}O_{0.86}Si(CH_2)_2PO(OH)_2]^g$			0.91	0.91	
	$C_{2.34}H_{8.29}O_{7.31}Si_{2.0}P^h$					4.2 (4.2)
EPSm2	$[(RO)_{4-n}O_{n/2}Si]_{2.0}[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OH)_2]^e$					
	$[(RO)_{0.48}O_{1.76}Si]_{2.0}[(RO)_{1.08}O_{0.96}Si(CH_2)_2PO(OH)_2]^f$	64	88	0.78 (R = H)		
	$[(EtO)_{0.41}(HO)_{0.07}O_{1.76}Si]_{2.0}[(HO)_{1.08}O_{0.96}Si(CH_2)_2PO(OH)_2]^g$			1.42	1.42	
	$C_{3.64}H_{11.32}O_{8.45}Si_{3.0}P^h$					3.3 (3.3)
EPSm3	$[(RO)_{4-2n}O_{n/2}Si]_{3.2}[(RO)_{3-n}O_{n/2}Si(CH_2)_2PO(OH)_2]^e$					
	$[(RO)_{0.24}O_{1.88}Si]_{3.2}[(RO)_{0.99}O_{1.01}Si(CH_2)_2PO(OH)_2]^f$	67	94	0.78 (R = H)		
	$[(HO)_{0.24}O_{1.88}Si]_{3.2}[(EtO)_{0.79}(OH)_{0.20}O_{0.89}Si(CH_2)_2PO(OH)_2]^g$			1.39	1.39	
	$C_{3.58}H_{10.92}O_{11.66}Si_{4.2}P^h$					2.6 (2.5)

[a] α = Overall % condensation of T^n sites. [b] β = Overall % condensation of Q^n sites. [c] –$PO(OH)_2$ loading calculated using the average formula. [d] Loading based on measured % P alone. [e] General formula of material. [f] Formula based on the measured (NMR) T^n/Q^n ratio, incorporating degrees of condensation. [g] Formula modified to account for experimental C : P ratio. [h] Average empirical formula.

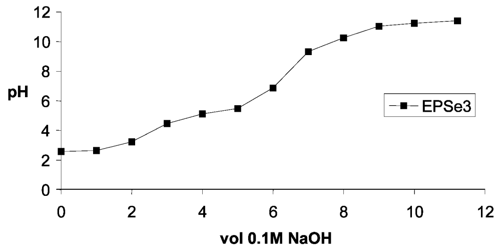

Fig. 3 Titration curve for EPSe3.

Table 5 NMR characterisation of the sodium phosphonate-modified silica Na_2EPSm3

NMR	Assignment	EPSm3	Na_2EPSm3
^{29}Si CP MAS	T^1	−64.76	−59.05
	T^2	−70.46	−66.35
	T^3	—	—
	Q^2	—	−91.98
	Q^3	−101.84	−101.34
	Q^4	−111.04	−110.60
^{31}P CP MAS		31.3	28.69
		21.1	—
^{13}C CP MAS		5.0	6.52
		19.8	17.23
		58.4 (trace)	62.18 (trace)

Table 6 Some details of the synthesis and chacterisation of VEPSm1 and VEPSm3

	Parent material	EPS used/g (P content/mmol)	V added/mmol	V content/mmol g^{-1}	V : P ratio	BET surface area/m^2 g^{-1}
VEPSm1	EPSm1	1.0688 (4.46)	6.00	1.08	1 : 4	3
VEPSm3	EPSm3	1.8192 (4.72)	6.00	0.96	1 : 5	245

Preparation of vanadium phosphonate-modified silicas

Phosphonic acid loading may be established by a combination of NMR and elemental analysis, as indicated above. We report here on some vanadyl phosphonate-modified silicas derived from the EPS series, and these are designated VEPS. For the preparation of VEPS, the strategy we found most successful was to first convert the EPS to the corresponding disodium phosphonate-modified silica, Na_2EPS.

This was achieved by treating powdered EPS with aqueous NaOH to pH 8.5 (see titration curve in Fig. 3) and the product subsequently thoroughly washed and dried. This step is important, as residual NaOH may interfere with subsequent applications. The solid state NMR data for Na_2EPSm3 prepared in this way are shown in Table 5. Most noteworthy is the shift in the phosphorus signal from ~32 ppm [–$PO(OH)_2$] to ~28 ppm [–$PO(ONa)_2$].

Na_2EPS m1 and Na_2EPSm3 became instantly coloured on treatment with aqueous vanadyl sulfate [$VO(SO_4)\cdot 5H_2O$]. The green vanadyl ethylphosphonate-modified silica, VEPS, thus obtained, was thoroughly washed with water and a range of other solvents. Details relating to the preparation and some properties of the VEPS materials are given in the Experimental section and in Table 6.

The vanadium loading was established by atomic absorption following metal ion liberation after stirring the VEPS materials in concentrated nitric acid.

Porosimetry studies show a slight decrease in surface area, but little change in the shape of the sorption–desorption isotherms on transformation of EPSm3 to VEPSm3 (Fig. 4).

Unsurprisingly, VEPSm1 remains non-porous like the parent EPSm1. It is noteworthy, however, that the vanadyl

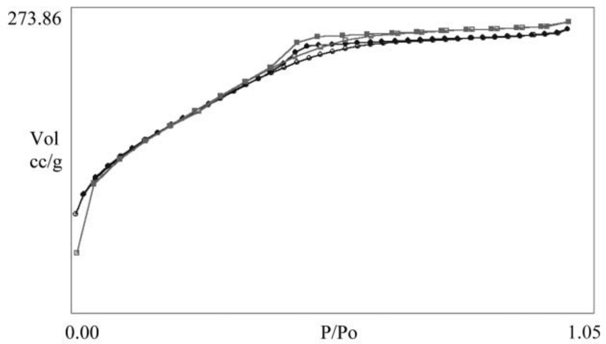

Fig. 4 Nitrogen sorption isotherms of EPSm3 (■) and VEPSm3 (●).

loading in VEPSm1 is similar to that in VEPSm3, despite differences in phosphonate loading and porosity.

During the last ten years or so, a number of groups (most notably Haushalter, Zubieta and co-workers[5]) have been investigating the coordination chemistry of vanadyl phosphonates. A number of structures have been fully elucidated from single crystal X-ray studies. Polymeric chain and layered structures with metal ions in octahedral or square pyramidal holes are commonly observed. Of course, since our materials are amorphous, it is more difficult to define the vanadyl connectivity, but the formation of strong V–O–P bonds is suggested by the instantaneous nature of the reactions of Na_2EPSm1 and Na_2EPSm3 with aqueous vanadyl sulfate $[VO(SO_4)\cdot5H_2O]$, as well as the requirement for harsh conditions to subsequently liberate vanadium species. In addition, the ^{31}P NMR signal in the spectra of VEPS is severely broadened compared to that in the spectra of the parent EPS materials, which is indicative of the close proximity of paramagnetic vanadium. The presence of VO^{2+} was confirmed by the appearance of strong EPR signals at g_{av} = 1.97 and 1.985 in the spectra of VEPSm1 and VEPSm3, respectively. The presence of a strong broad band associated with the silica matrix in the region of 960 cm^{-1} masked the characteristic vanadyl vibrational mode at ~995 cm^{-1} in the IR spectra of the VPES.

The diffuse reflectance UV-Vis spectra of VEPSm1 and VEPSm3 were identical and had the expected bands for d–d and charge transfer transitions associated with the d^1 VO^{2+} ion (Table 7). We note that the large pore vanadosilicates AM-13 and AM-14, prepared with $[VO(SO_4)\cdot5H_2O]$,[6] showed bands at 600, 420–430, 320 and 270 nm, attributed to hexacoordinate $V^{IV}O$ and some tetrahedral V(v), in their UV-Vis spectra. The appearance of a band at 340 nm in the spectra of the VEPS materials indicates that some tetrahedral V(v) may be present, while the bands in the visible region are attributed to the VO^{2+} species.[7] The presence of some V(v) was confirmed by the appearance of a broad asymmetric signal (at 200 to −200 ppm $W_{1/2}$ = 53 kHz) in the solid state ^{51}V NMR spectrum of VEPSe3. Although a number of vanadyl phosphonate materials have been structurally characterised, DRUV-Vis data on these was not, as far as we are aware, reported.

Catalytic oxidation of *cis*-cyclooctene using hydrogen peroxide with VEPSm3 as catalyst

The partial oxidation of organic substrates assisted by heterogeneous catalysts represents an important clean route to functionalised organic molecules and recent progress in this area has been reviewed.[8] In the work reported here, catalytic oxidation of *cis*-cyclooctene was assessed using the VEPSm3 material as catalyst and aqueous hydrogen peroxide (30%) as oxidant. Various recent reports indicate low activity and leaching problems with some porous metal silicates[8,9] and silica-supported metal complexes when using aqueous hydrogen peroxide, although better results were obtained with *tert*-butyl hydroperoxide. In our case, we expected leaching to be minimised by strong metal phosphonate complexation. The results are summarised in Table 8.

Table 7 DRUV-Vis data for VEPS materials

	λ/nm
VEPSm1	230, 280, 340, 580, 760
VEPSm3	230, 280, 340, 580, 760
$VOSO_4\cdot5H_2O$	240(s), 640(m), 760(s)

Table 8 Oxidations catalysed by VEPSm3

Organic substrate	Oxidant	% Epoxide
cis-Cyclooctene	30% H_2O_2 (aq)	47, 49[a] 42[b] 0[c]

[a] Reaction conditions: 20 mmol organic substrate, 1.5 mol% VEPS catalyst (based on V loading), 10 ml *tert*-butanol, 22 mmol oxidant (added over a 15 min period); reaction time/temperature 0.5 h/60 °C. [b] Second run with catalyst filtered from first run reaction mixture at room temperature and treated with fresh reagents, as above. [c] Leaching test—activity of hot filtrate exposed to fresh reagents. Product analysis by ^{13}C and ^{1}H NMR. Blank reactions, including one with Na_2EPSm3, produced no epoxide.

The first positive observations were that colourless solutions could be separated from the catalyst at the end of the reactions indicating little, if any, leaching of vanadium species. There was no measurable leached vanadium as determined by a hot filtration test. In contrast, Neumann *et al.* reported that the material $VO_{2.5}$–$3SiO_2$ dissolved in the homogeneous phase (30% H_2O_2–acetone–cyclooctene mixture).[9] Secondly, we see a fairly useful (~48%) conversion of cyclooctene to the epoxide, while zero conversion was reported for the $VO_{2.5}$–$3SiO_2$/30% H_2O_2 system.[9] The immobilised vanadium is obviously providing the catalytic activity in the VEPSm3 system since zero conversions were observed for blank reactions using Na_2-EPSm3 instead of VEPSm3, and for filtrates from VEPSm3 reaction mixtures. Extensive studies of the catalytic activity of these and other metal derivatives of the phosphonate-modified silicas we describe here are in progress and will be reported in due course.

Conclusions

We have devised synthetic strategies to mesoporous phosphonic acid-modified silicas with relatively high phosphonic acid loading and shown a clear relationship between loading and porosity. The disodium salts of these phosphonic acid-modified silicas were then prepared and characterised, and subsequently used to incorporate strongly bound transition metal ions. To our knowledge, these materials represent the first examples of metal phosphonate-modified silicas.We have also demonstrated that our vanadyl phosphonate-modified silicas are active catalysts for the oxidation of cyclic olefins to epoxides using the clean oxidant hydrogen peroxide.

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 stored over molecular sieves. The reagent $(EtO)_3$-$Si(CH_2)_2PO(OEt)_2$ was synthesised according to the literature method.[10] The compounds $Si(OEt)_4$, TEOS, $[VO(SO_4\cdot5H_2O]$, *cis*-cyclooctene and 30% aqueous hydrogen peroxide are commercially available.

Solution state NMR spectra were recorded from $CDCl_3$

solutions using a 270 MHz JEOL spectrometer and Bruker 250, 400 and AMX 600 MHz spectrometers. All solid state NMR spectra [^{29}Si CP MAS and SPE MAS (59.6 MHz), ^{13}C CP MAS (75.5 MHz), ^{31}P CP MAS (121.5 MHz)] were recorded on a Bruker MSL 300 MHz spectrometer (spinning speed: P 9 kHz, Si 5.5 kHz, C 6 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. Elemental analyses 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.[11] Pore size distributions in the mesopore region were determined by the BJH method.[12] The de Boer t-method[13] was used to evaluate the micropore volume.

Synthesis

General procedure for the synthesis of the EPES materials. The reagents TEOS and $(EtO)_3Si(CH_2)_2PO(OEt)_2$, were dissolved in an approximately equal volume of ethanol or methanol, as appropriate, under nitrogen. The mixtures were stirred for 10 min and then aqueous 1 M HCl added (the volume of HCl solution added was 0.25 times the volume of alcohol used). The reaction mixtures were stirred for an hour, after which clear solutions had formed. The sols were then allowed to stand in an oven at 60 °C for 16 days, after which the solvents had evaporated and hard transparent monophasic glasses were formed. These were crushed into fine powders and washed consecutively with water, ethanol and ether, then dried under vacuum (0.01 mm Hg) at room temperature for 12 h and subsequently under vacuum (0.001 mm Hg) at 120 °C for 12 h.

General procedure for the hydrolysis of the EPES materials. The EPES powders and concentrated HCl (1.0 g to 10 cm^3) were refluxed for 24 h. The mixtures were filtered and washed with water until the washings were neutral, and then further washed with ethanol and ether. The powders were then dried under vacuum (0.01 mm Hg) at room temperature for 12 h and subsequently under vacuum (0.001 mm Hg) at 120 °C 12 h.

General procedure for the preparation of VEPSm. Dried EPSm1 or EPSm3 were suspended in 15 ml of distilled water (see Table 6 for quantities). Aqueous 1 M NaOH was added slowly and dropwise to pH 8.5 in order to form the disodium phosphonate salt. When the pH of the solution reached 8.5, the salts were filtered off and washed with water until the washings were neutral. The product was further washed with ethanol and ether, finally, the white solid was dried under vacuum (0.01 mm Hg) at room temperature for 12 h and subsequently under vacuum (0.001 mm Hg) at 120 °C 12 h. BET surface area for Na_2EPSm 3 253 m^2 g^{-1}. See Table 5 for solid state NMR data on Na_2EPSm3.

The disodium phosphonate Na_2EPSm materials obtained in this way were suspended in 15 ml of distilled water, and $[VO(SO_4)\cdot5H_2O]$ was added in excess (the V : P ratio was ~1.3 : 1). The reaction mixtures were stirred at room temperature for 17 h. The turquoise materials were filtered off and washed with excess water (0.5 L g^{-1}) at room temperature, then stirred in water at 65 °C for 15 min to remove any trace of weakly bound vanadium species. The materials were finally washed with ethanol and ether, then dried under vacuum (0.01 mm Hg) at room temperature for 12 h and subsequently under vacuum (0.001 mm Hg) at 120 °C 12 h. See Tables 6 and 7 for characteristic features.

General procedure for catalysis. The reaction mixtures including Bu^{t}OH, organic substrate and the VEPSm3 catalyst (see Table 8) were combined under nitrogen and heated to 60 °C. The oxidant solutions were added dropwise. After 15 min, the reaction mixture was filtered and the liquid phase extracted with ether. The organic layer was dried over $MgSO_4$, the solvent evaporated and the composition of the residual mixture evaluated by NMR. The filtered catalyst continued to be active when treated with a second batch of reagents. Hot filtrates from the reaction mixtures were found to be inactive when treated with fresh reagents. Blank reactions were carried out without added catalyst and also with added Na_2EPSm3. In both cases, substrate conversion was 0%.

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