

Ordered SBA-15 mesoporous silica containing phosphonic acid groups prepared by a direct synthetic approach

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Highly ordered hydrothermally stable SBA-15 mesoporous silica containing phosphonic acid groups are synthesised for the first time by using amphiphilic block copolymers as the structure-directing agents.

Surfactant-templated mesoporous hybrid materials constitute a very exciting field in materials chemistry.^{1–8} This class of materials has numerous potential applications^{9–12} due to their high surface areas and their narrow pore size distributions as well as the diversity of the functional groups which they can contain. Recently Stucky *et al.*⁸ have published the preparation of ordered SBA-15 mesoporous silica containing sulfonic acid groups using the direct synthetic approach. That prompted us to report in this paper the results that we obtained by the same route concerning the preparation and the physicochemical characteristics of periodic hybrid mesoporous materials containing phosphonic acid groups based on the co-condensation of tetraethylorthosilicate (TEOS) and an appropriate organotrimethoxysilane in the presence of triblock copolymers as the structure-directing agent under acidic conditions.

First we prepared SBA-15 mesoporous silica containing phosphonic acid diethyl ester groups. In a typical experiment 4.0 g of EO₂₀PO₇₀EO₂₀ was dissolved in an aqueous HCl solution (160 ml, pH ≈ 1.5). This solution was added to a mixture of 8.4 g of TEOS and of 1.4 g of trimethoxysilylpropyldiethylphosphonate **1** at ambient temperature. The mixture was stirred for 3 h giving rise to a microemulsion. After heating this perfectly transparent solution at 60 °C, a small amount of NaF (75.4 mg) was added with stirring to induce hydrolysis and polycondensation. The mixture was stirred at 60 °C for 48 h. The resulting solid was filtered off and washed. The surfactant was then removed by hot ethanol extraction in a Soxhlet apparatus affording the X[PO(OEt)₂] material in 95% yield. The molar composition of the reaction mixture was: 0.04 F⁻: 1 TEOS: 0.11 **1**: 0.02 P 123: 0.12 HCl: 220 H₂O. Some relevant physicochemical data for X[PO(OEt)₂] are given in Table 1. The CP MAS ³¹P NMR spectrum of X[PO(OEt)₂] displays one sharp signal ($\Delta\nu_{1/2} = 720$ Hz) which was attributed to the phosphonic acid diethyl ester group. Further indication of the presence of diethyl ester group was given by CP MAS ¹³C NMR spectroscopy with the signal at 63 ppm attributed to PO(OCH₂) groups. From elemental analysis, the content of functional groups was found to be of 1.33 mmol g⁻¹

while the theoretical value was 1.29. The powder X-ray pattern (Fig. 1a) exhibits an intense diffraction peak corresponding to d_{100} spacing and two weak peaks (d_{110} 61.5 Å and d_{200} 52.5 Å) which are characteristic of a 2D hexagonal structure. Interestingly, no significant change was observed for the XRD pattern recorded eight months later of the material which was stored in air (Fig. 1b), indicating a very stable structure. Further evidence for a highly ordered 2D hexagonal structure was provided by the transmission electron microscopy (TEM) images shown in Fig. 2. The N₂ adsorption–desorption isotherm for X[PO(OEt)₂] is displayed in Fig. 3. The sample showed type IV isotherm, characteristic of mesoporous materials with a narrow pore size distribution.

Two routes gave rise to mesoporous silica containing phosphonic acid groups. In both cases, silylation of SiOH groups was first achieved by treating the mesoporous solid with Me₃SiCl in toluene heated under reflux for 12 h in order to avoid side reactions between the phosphonic acid groups and the surface SiOH. Acid catalysed hydrolytic desalkylation¹³ was then accomplished by treating the resulting solid X_{Si}[PO(OEt)₂] with a 12 M aqueous solution of HCl for 24 h under reflux (route

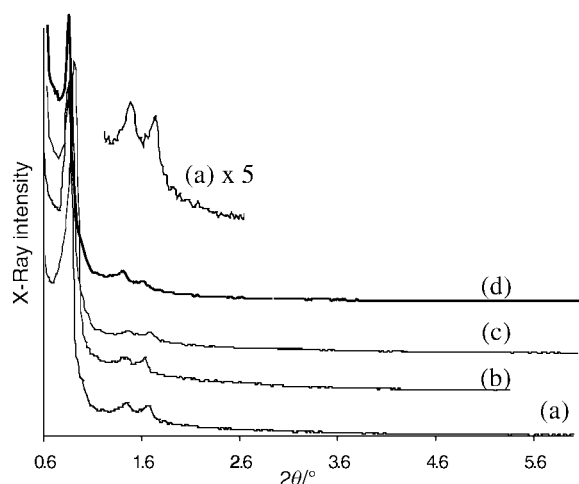


Fig. 1 XRD patterns for (a) X[PO(OEt)₂]; (b) for X[PO(OEt)₂] after eight months; (c) for X_{Si3a}PO(OH)₂; (d) for X_{Si3b}PO(OH)₂.

Table 1 Physicochemical properties of mesoporous SBA-15 silica containing phosphonic acid diethyl ether or phosphonic acid groups

Sample	CP MAS ³¹ P NMR δ /ppm	Mmol g ⁻¹ (theor. value)	S _{BET} /m ² g ⁻¹	D _p /Å	V _p /cm ³ g ⁻¹	d ₁₀₀ /Å	Wall ^d thickness/Å
X[PO(OEt) ₂]	33.5	1.33 ^a (1.29)	696	75	1.03	106	47
X _{Si3a} [PO(OH) ₂]	32.5	1.08 ^b	618	70	1.03	105	52
X _{Si3b} [PO(OH) ₂]	33.2	1.08 ^b	580	71	0.89	105	51

^a Calculated from elemental analysis. ^b Calculated from acid–base titration. ^c Calculated from the adsorption branch. ^d Calculated from $a -$ pore size ($a_0 = 2d_{100}/\sqrt{3}$).

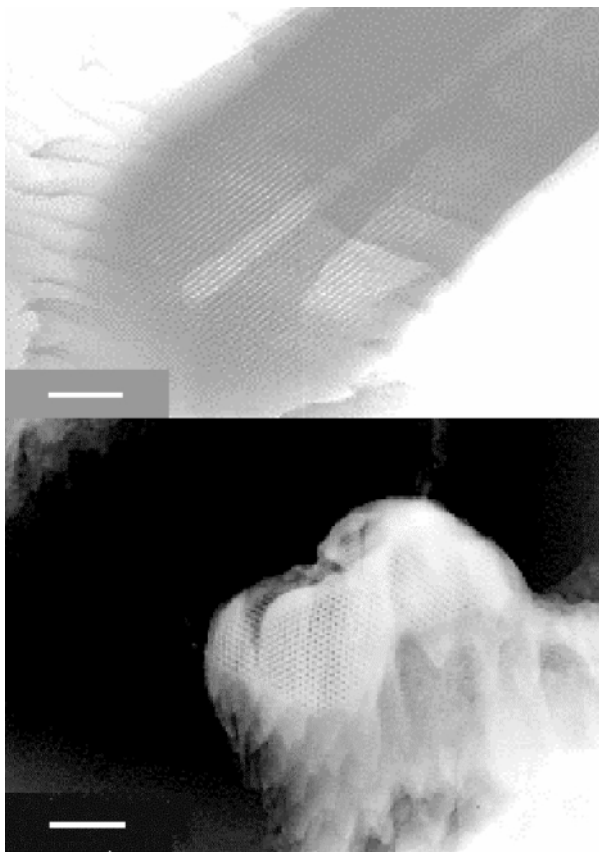


Fig. 2 TEM images of the X[PO(OEt)₂] material: (bottom) in the direction perpendicular to the pore axis; (top) in the direction of the pore axis. The images were recorded on a JEOL JEM 200CX transmission electron microscope. Scale bar = 100 nm.

a) giving rise to X_{Si}a[PO(OH)₂]. The second route (route b) consisted of the preparation of the bis(trimethylsilyl)phosphonate which can then be smoothly converted to phosphonic acid on contact with neutral H₂O at room temperature¹⁴ thus avoiding the harsh reaction conditions of preparation of X_{Si}a[PO(OH)₂]. For this purpose, refluxing X_{Si}b[PO(OEt)₂] with 2 equiv. of Me₃SiBr in toluene for 24 h afforded X_{Si}b[PO(OH)₂] after addition of H₂O. Some relevant physicochemical data for both materials are given in Table 1. It is worth noting that all the data are very similar. The CP MAS ³¹P NMR spectra of both materials display only one sharp signal ($\Delta v_{1/2} = 640$ Hz), indicating the absence of reaction between the phosphonic acid groups and the surface SiOH. Though the ³¹P NMR chemical shift of the PO(OH)₂ groups is unfortunately very close to that of PO(OEt)₂ groups, evidence for the complete formation of phosphonic acid groups in both cases was given by CP MAS ¹³C NMR spectroscopy with the disappearance of the signal attributed to the PO(OCH₂) groups. Furthermore, the exact amount of phosphonic acid groups was measured by acid–base titration. For this determination, the materials were first placed in an aqueous Li₂CO₃ solution (pH 8) in which an ion exchange occurred quantitatively (³¹P NMR, $\delta 26$ ppm ($\Delta v_{1/2} = 320$ Hz), Li/P ratio, 1.95 from elem. anal.). The filtrate was then treated with an excess of an aqueous HCl solution. From the acid–base conductimetric titration, the amount of PO(OH)₂ groups per gram was found to be 1.08 mmol g⁻¹ taking into account the same titration from X_{Si}b[PO(OEt)₂] as a blank. The N₂ adsorption–desorption isotherms are of type IV in both cases with a very similar narrow pore size distribution (Fig. 3). Figs. 1c and 1d show the powder X-ray patterns of respectively X_{Si}a[PO(OH)₂] and X_{Si}b[PO(OH)₂]. They are very similar to

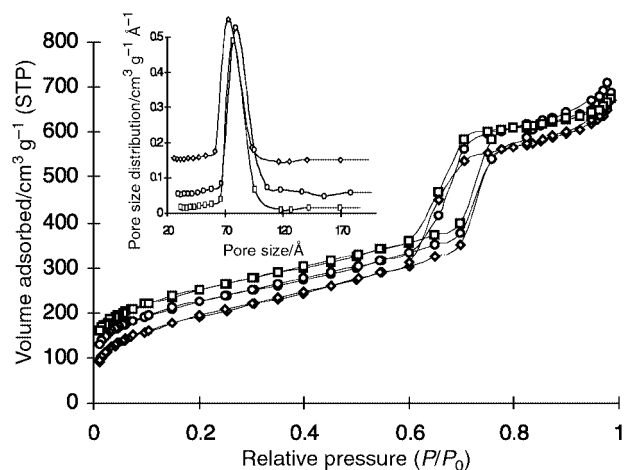


Fig. 3 Nitrogen adsorption–desorption isotherm and BJH pore size distribution plot (inset) of XPO(OEt)₂ (□), X_{Si}aPO(OH)₂ (○) and X_{Si}bPO(OH)₂ (◇). To allow a better comparison, the data for X_{Si}aPO(OH)₂ and XPO(OEt)₂ were shifted by 50 and 100 cm³ g⁻¹ respectively.

that of X[PO(OEt)₂] (Fig. 1a) indicating that the mesoscopic ordering completely survives both post syntheses. Thus, it can be concluded that the structures of these materials are hydrothermally stable as X_{Si}a[PO(OH)₂] was treated with a 12 M HCl aqueous solution heated under reflux for 24 h. This is a specificity of SBA-15 materials.^{8,15,16} They are also stable under basic conditions (pH 8). Finally, phosphonic acid groups are interesting in that they allow the incorporation of numerous transition metals which should have good potential in catalysis. As example, we show that treatment of X_{Si}a[PO(OH)₂] with a THF solution of nickel acetylacetonate (2 equiv. per PO(OH)₂ group) heated under reflux for 12 h yielded quantitatively the nickel salts (one signal at 22 ppm in CP MAS ³¹P NMR).

In summary, we have developed two routes in several steps giving rise to the same highly ordered mesoporous hybrid materials containing free phosphonic acid groups. This study constitutes, to the best of our knowledge, the first example of ordered mesoporous silica containing such a functional group.

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